REACTIONS OF ALKANES:

CONTENTS

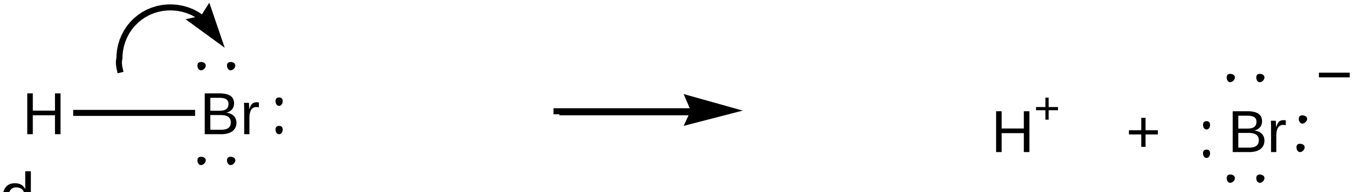
RADICALS

Sources include:

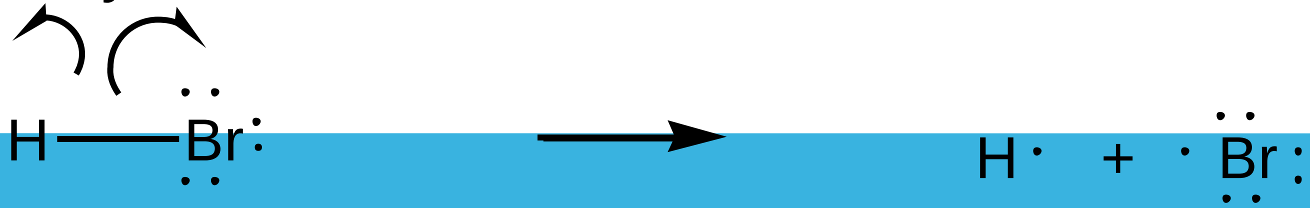
- Hydrogen peroxide
- Alkyl peroxides
- Light causes homolysis of the weak O-O bond

HETEROLYSIS & HOMOLYSIS

Heterolytic bond cleavage or heterolysis



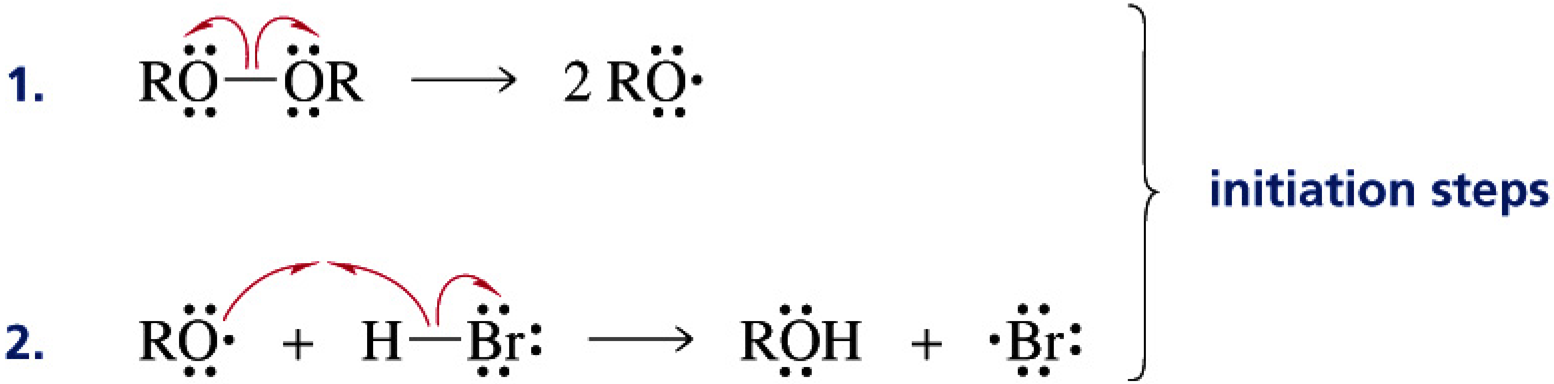
Homolytic bond cleavage or homolysis



Homolysis produces **radicals**, which are very reactive species

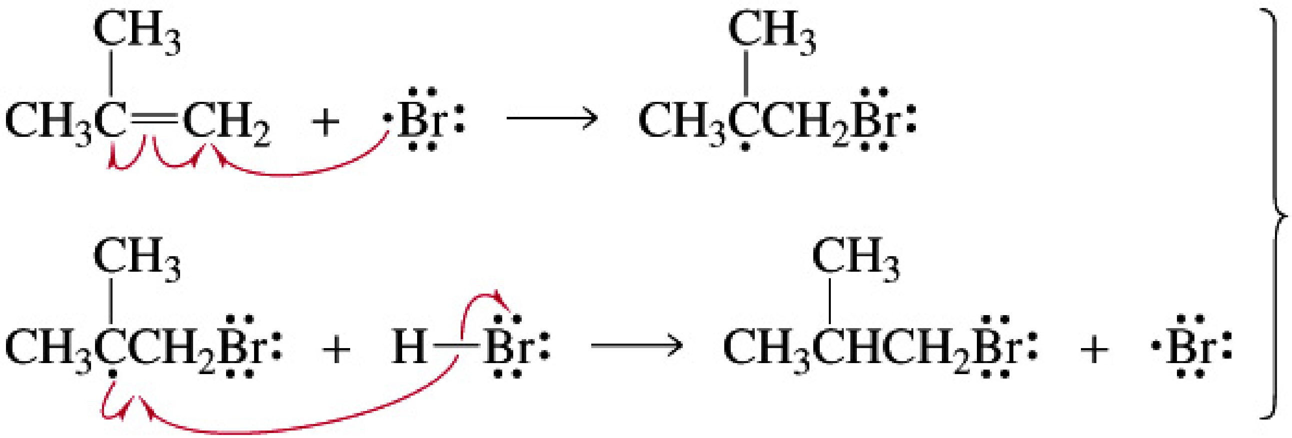
RADICAL CHAIN REACTIONS

Initiation turns stable species into radicals by breaking a bond.



RADICAL CHAIN REACTIONS

Propagation causes products to form without resulting in net consumption of radicals.
(production = consumption)



3. $\mathrm{CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 + \cdot\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\cdot}{C}}CH_2\ddot{\underset{\cdot\cdot}{Br}}:}$

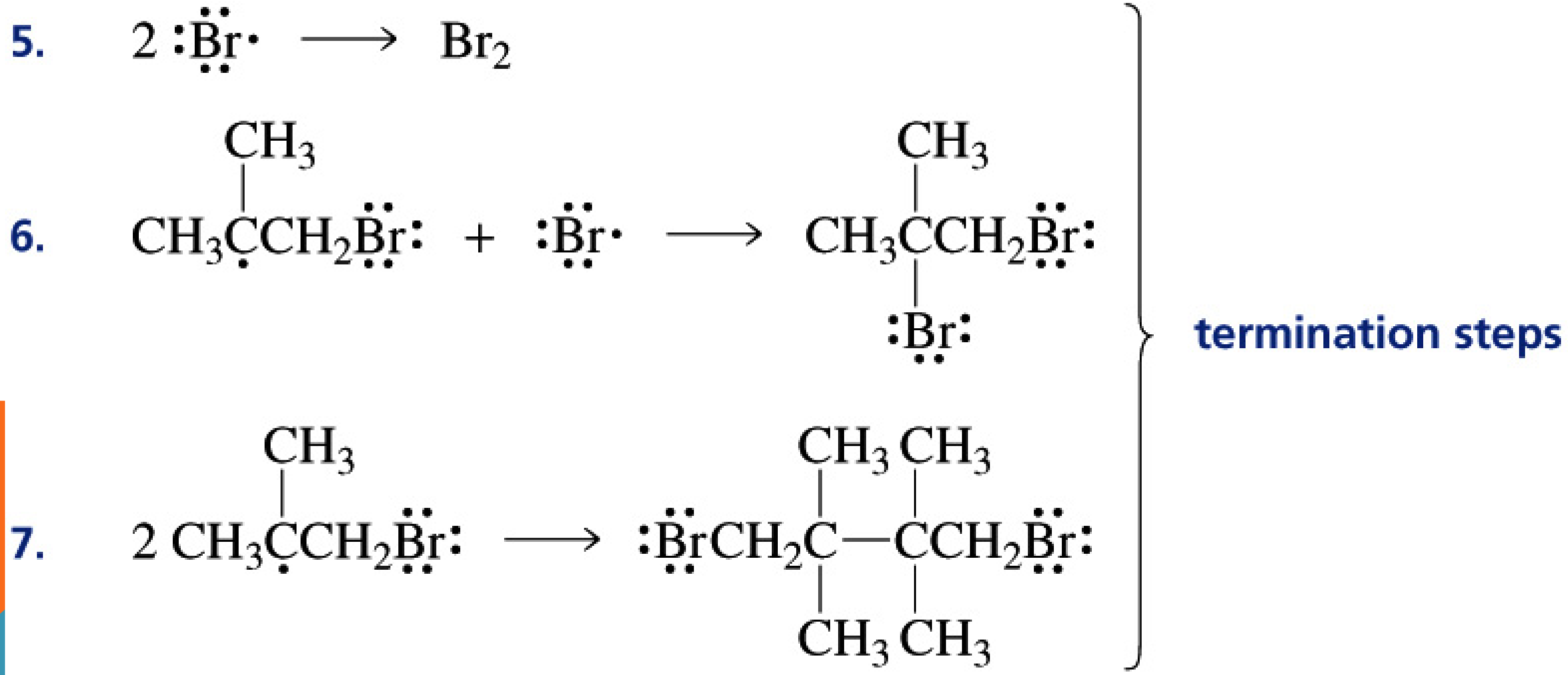
4. $\mathrm{CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\cdot}{C}}CH_2\ddot{\underset{\cdot\cdot}{Br}}: + H{-}\ddot{\underset{\cdot\cdot}{Br}}: \longrightarrow CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\ddot{\underset{\cdot\cdot}{Br}}: + \cdot\ddot{\underset{\cdot\cdot}{Br}}:}$

propagation steps

RADICAL CHAIN REACTIONS

Termination results in net radical destruction.

Generally occurs when reactants are used up.



5. $2\,:\!\ddot{\underset{..}{Br}}\cdot \longrightarrow Br_2$

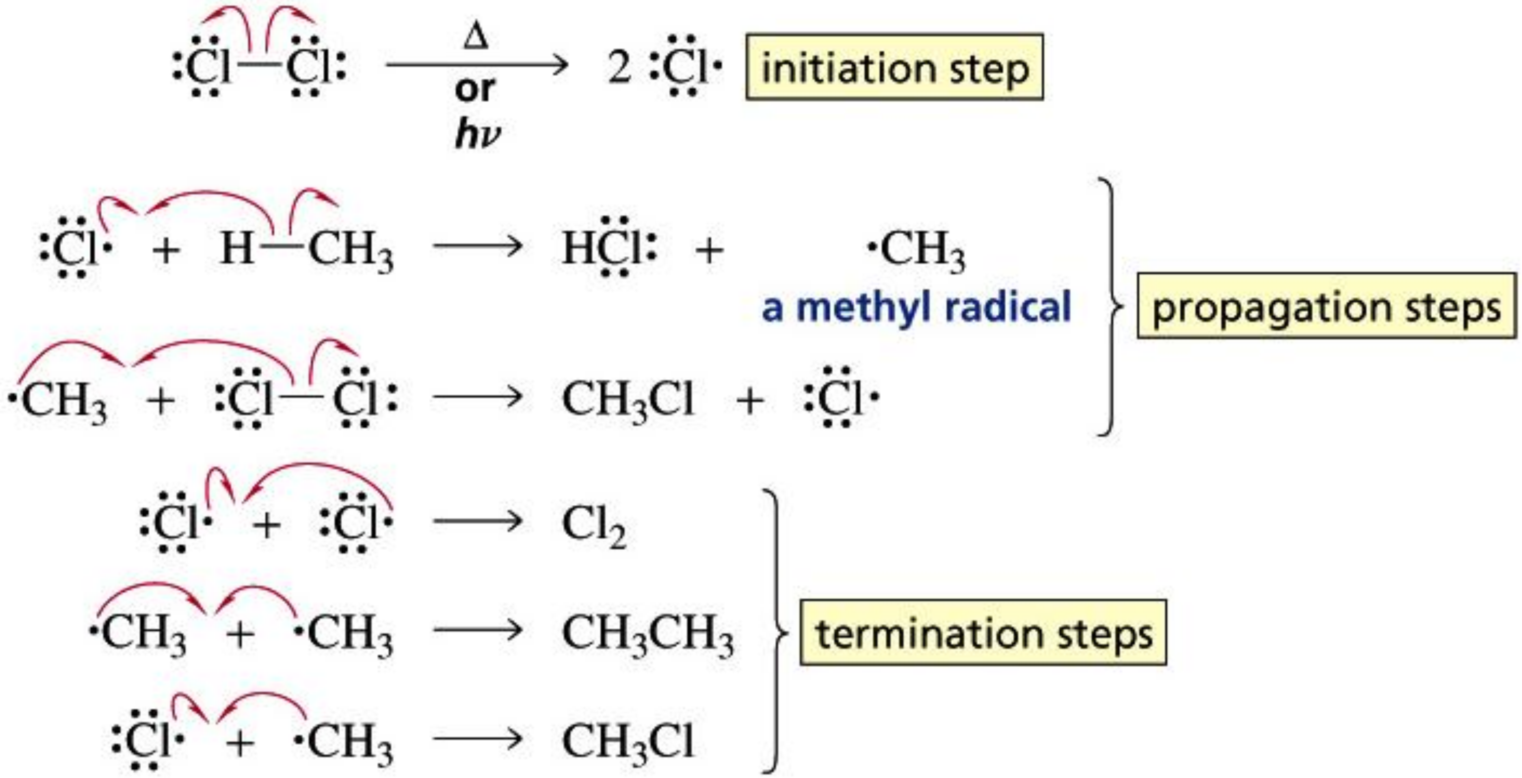
6. $CH_3\overset{CH_3}{\underset{\cdot}{C}}CH_2Br: + :\!Br\cdot \longrightarrow CH_3\overset{CH_3}{\underset{:Br:}{C}}CH_2Br:$

7. $2\,CH_3\overset{CH_3}{\underset{\cdot}{C}}CH_2Br: \longrightarrow :BrCH_2\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}CH_2Br:$

termination steps

CHLORINATION AND BROMINATION OF ALKANES

mechanism for the monochlorination of methane



PRODUCT DISTRIBUTION

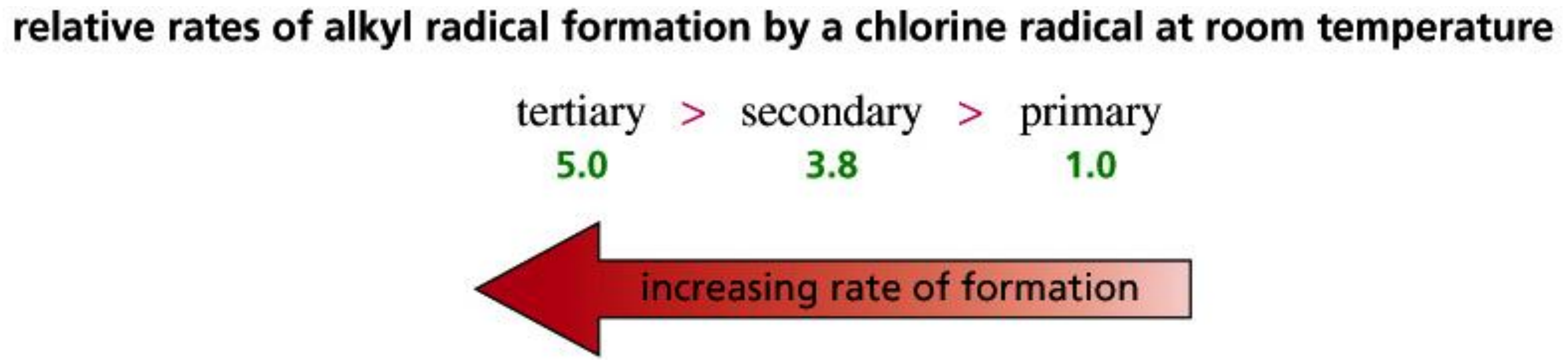
$$CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2CH_2CH_2Cl + CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3 + HCl$$

butane

1-chlorobutane
expected = 60%
experimental = 29%

2-chlorobutane
expected = 40%
experimental = 71%

CHLORINATION RATES



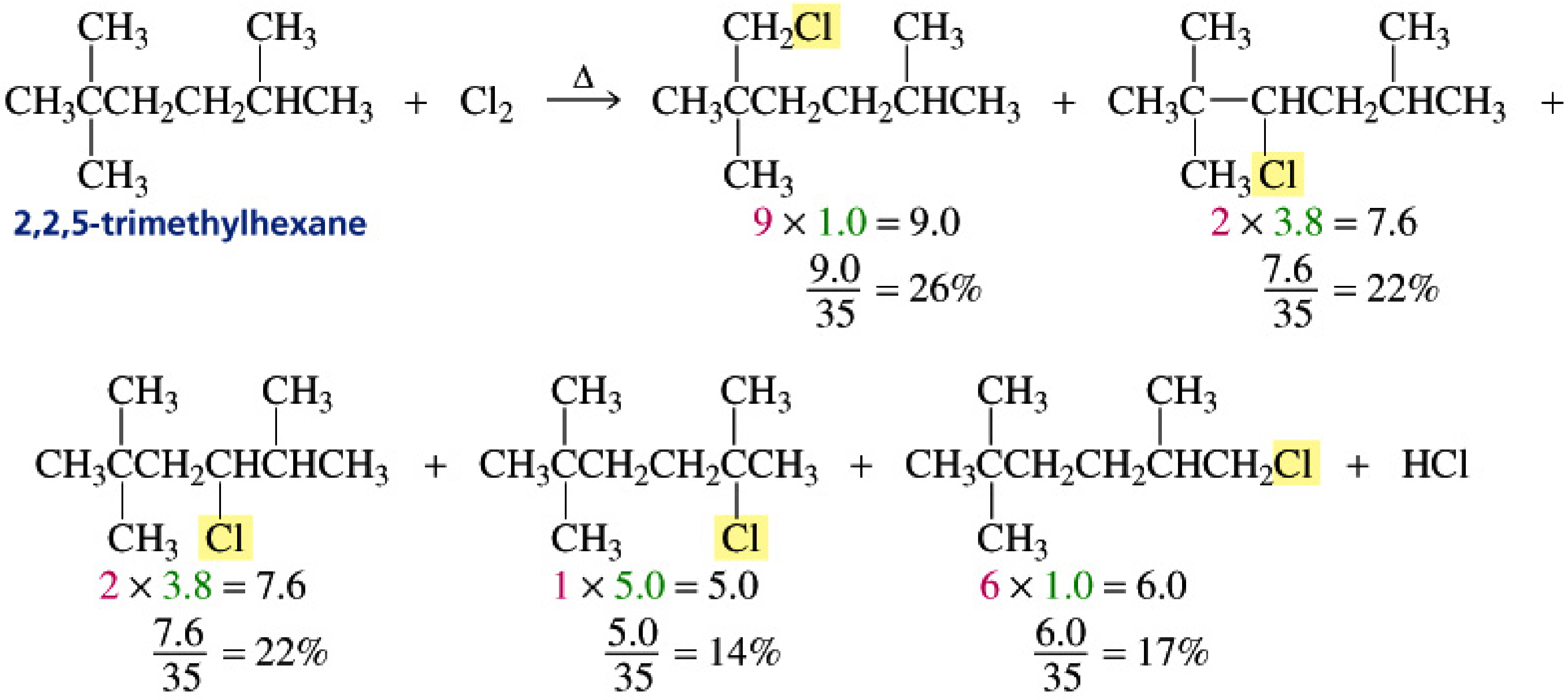
relative rates of alkyl radical formation by a chlorine radical at room temperature

tertiary > secondary > primary

5.0 3.8 1.0

increasing rate of formation

CHLORINATION PRODUCT DISTRIBUTION



$$9 \times 1.0 = 9.0 \qquad \frac{9.0}{35} = 26\%$$

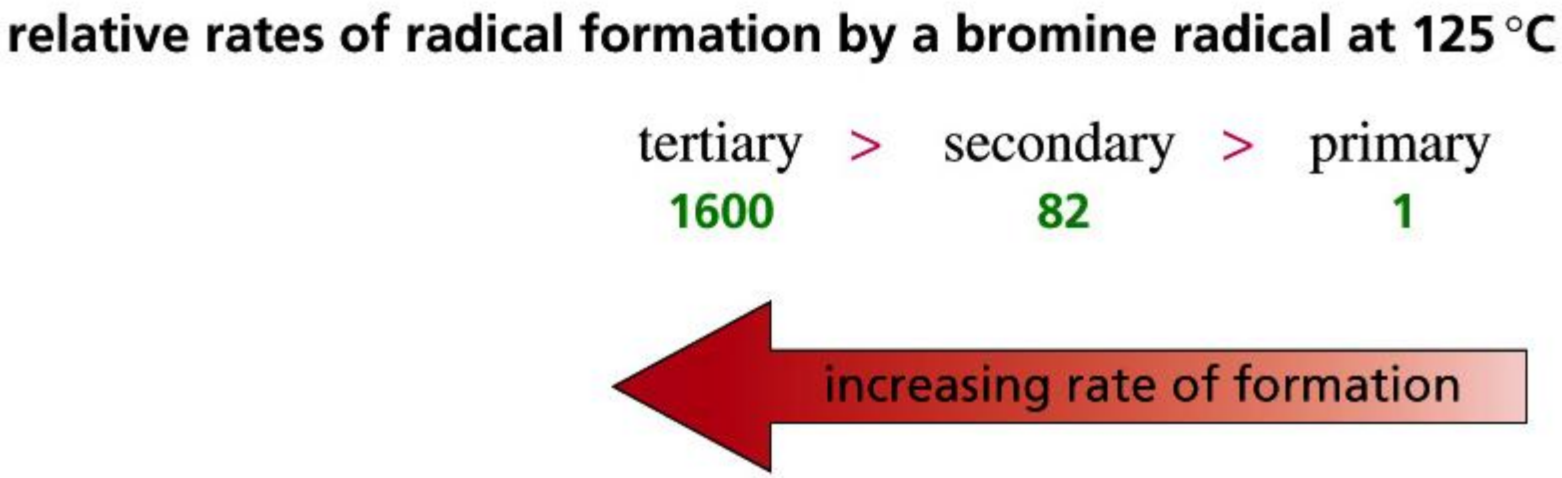
$$2 \times 3.8 = 7.6 \qquad \frac{7.6}{35} = 22\%$$

$$2 \times 3.8 = 7.6 \qquad \frac{7.6}{35} = 22\%$$

$$1 \times 5.0 = 5.0 \qquad \frac{5.0}{35} = 14\%$$

$$6 \times 1.0 = 6.0 \qquad \frac{6.0}{35} = 17\%$$

BROMINATION RATES



relative rates of radical formation by a bromine radical at 125 °C

tertiary	>	secondary	>	primary
1600		82		1

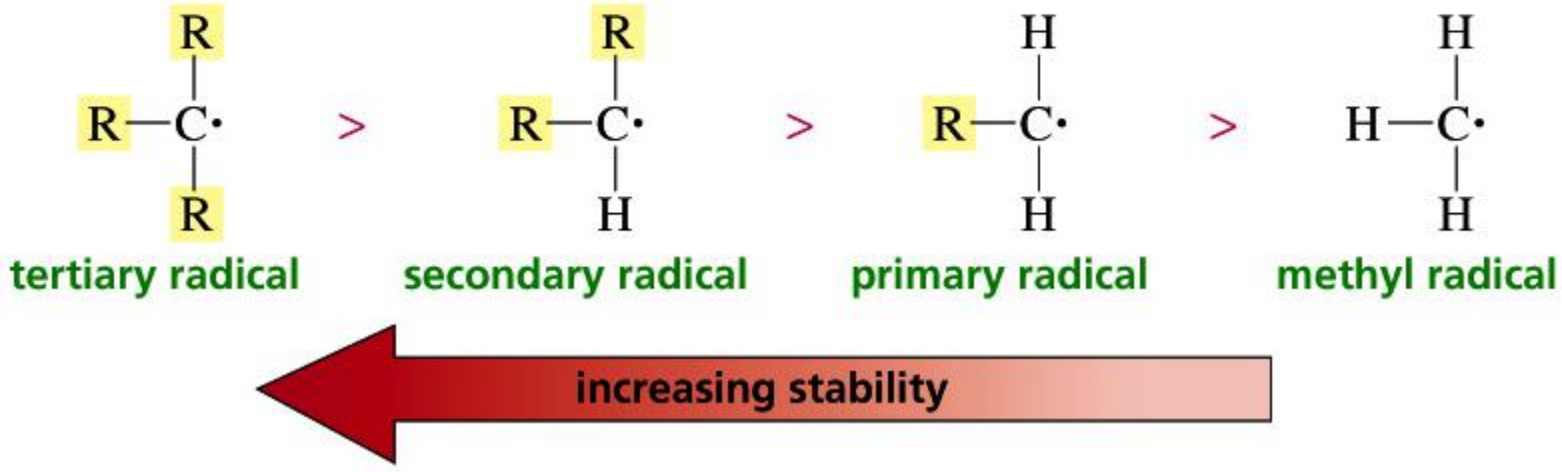
REACTIVITY–SELECTIVITY PRINCIPLE

The very reactive chlorine atom will have lower selectivity and attack pretty much any hydrogen available on an alkane

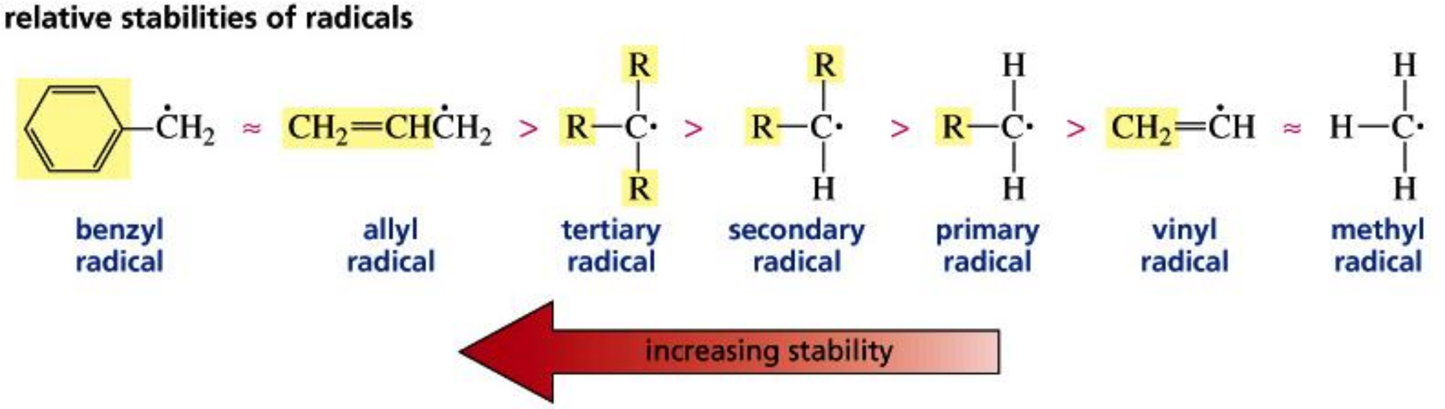
The less reactive bromine atom will be more selective and tends to react preferentially with the easy targets, i.e. benzylic/allylic > 3° > 2° > 1°

RADICALS

Stability of alkyl radicals is similar to stability of carbocations



CRUDE RADICAL STABILITY INDEX


relative stabilities of radicals

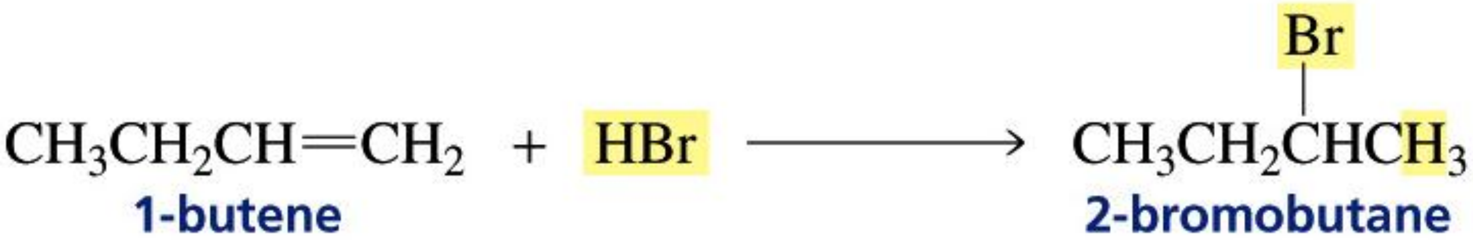
Add 1 for each attached carbon.

Add 3 for adjacent double bond or phenyl ring.

Radical equally stable on double bond carbon as on single bonded carbon

Profile similar to carbocations but resonance contributes more to radical stability, and radical is OK on C=C.

ADDITION OF RADICALS



$$CH_3CH_2CH{=}CH_2 + HBr \longrightarrow CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3$$

1-butene 2-bromobutane

Markovnikov Addition

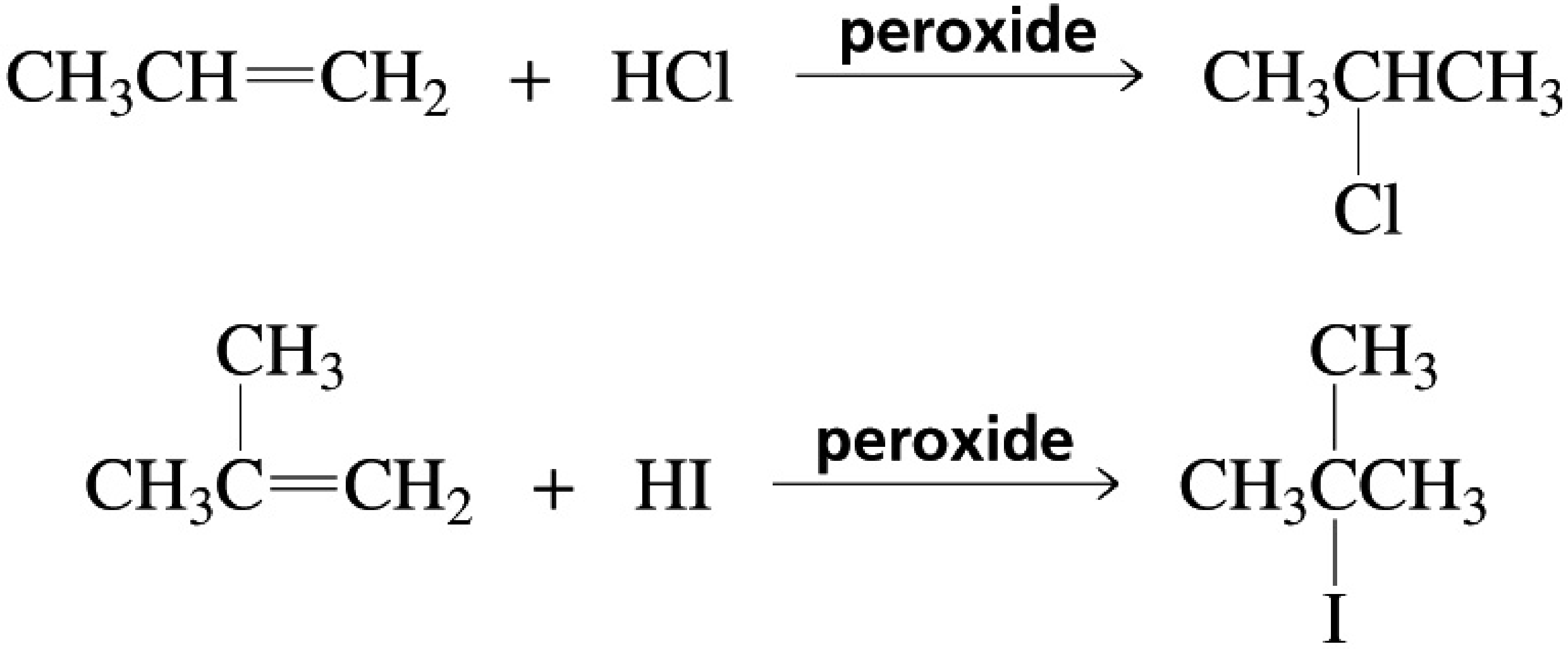
$$CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2CH_2Br$$

1-butene 1-bromobutane

Anti-Markovnikov Addition

Source of confusion regarding addition of HBr for years; **can’t** do ionic product analysis with radicals!!!

RADICAL ADDITION IS UNIQUE TO HYDROGEN BROMIDE



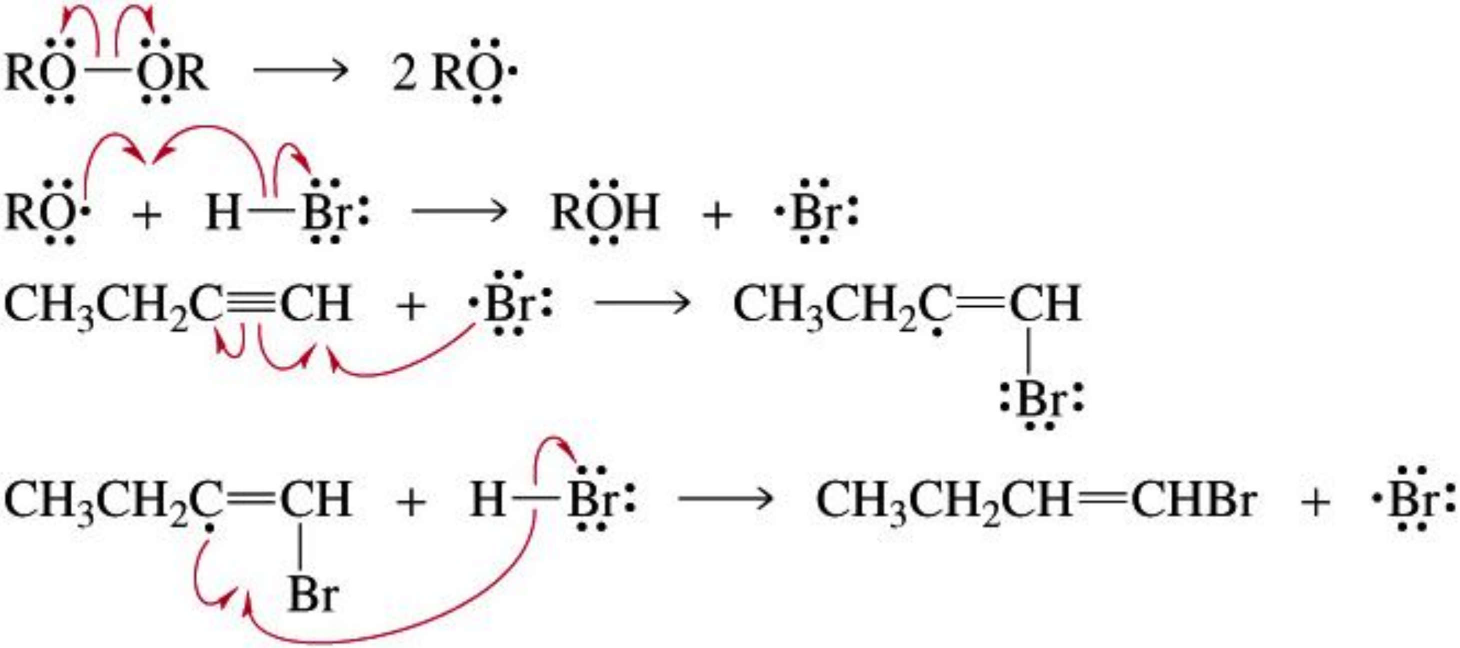
$$CH_3CH{=}CH_2 + HCl \xrightarrow{\text{peroxide}} CH_3\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3$$

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 + HI \xrightarrow{\text{peroxide}} CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle I}{|}}{C}}CH_3$$

HBr and peroxide goes anti-Markovnikov!

HYDROGEN HALIDE ADDITION IN THE PRESENCE OF PEROXIDE

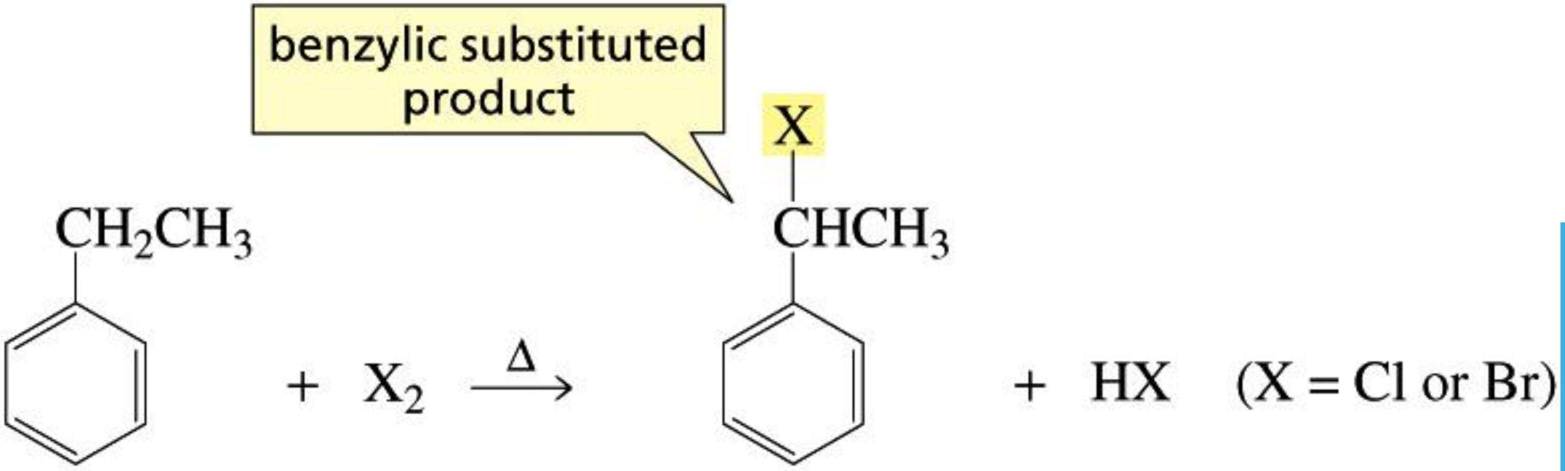
Hydrogen peroxide has same effect on hydrogen bromide addition to an alkyne as to an alkene (reversed regioselectivity).



BENZYLIC/ALLYLIC RADICALS

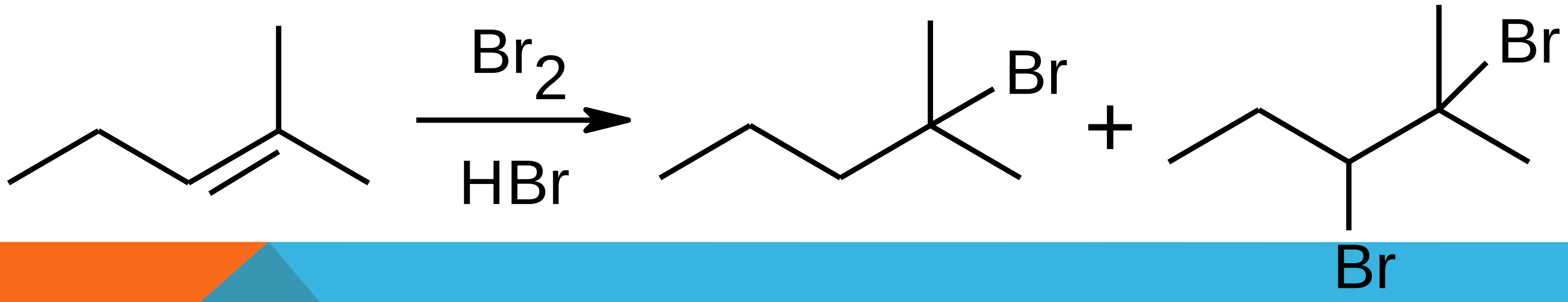
Benzylic and allylic radicals are even more stable than tertiary alkyl radicals

It should be easy for a halogen radical to abstract a benzylic or allylic hydrogen



BENZYLIC/ALLYLIC RADICALS

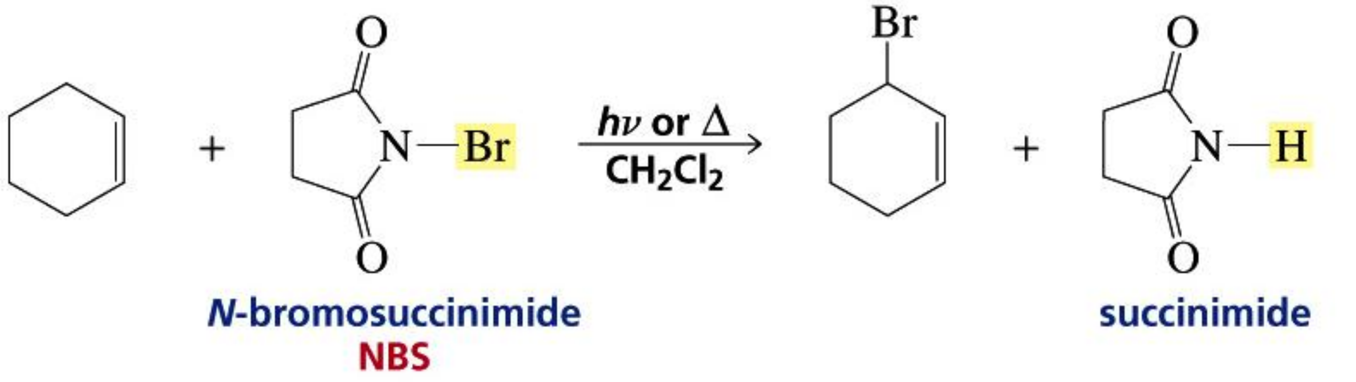
Problem in making allylic radical is the greater likelihood that HBr or Br_2 will add electrophilically to the double bond rather than making the allylic radical.



BENZYLIC/ALLYLIC RADICALS

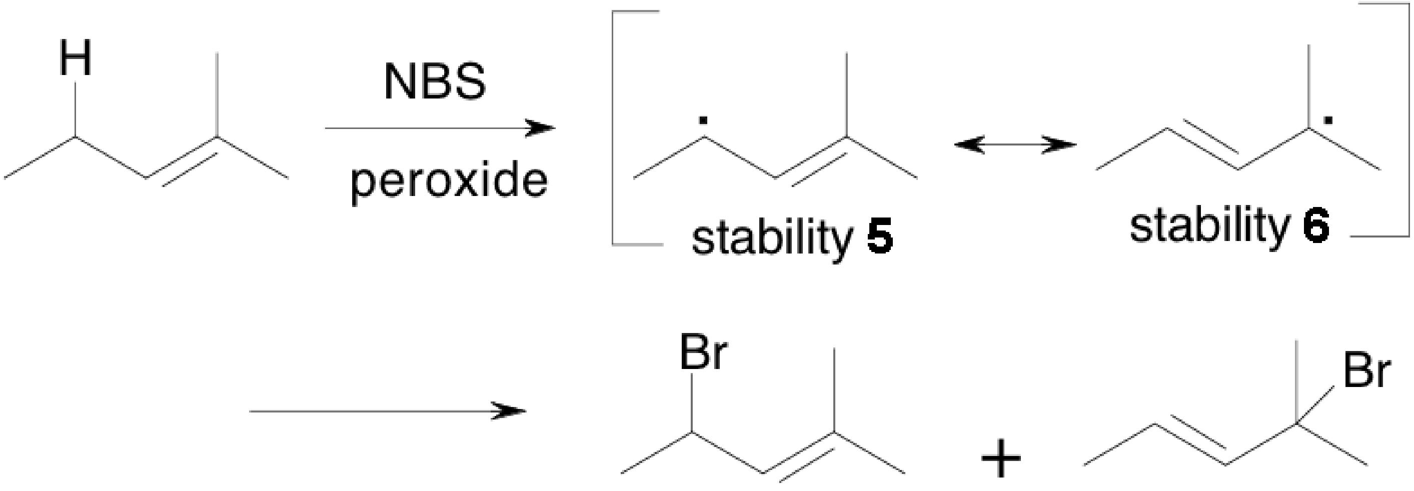
Problem solved with *N*-bromosuccinimide (NBS) is a good reagent for supplying low concentrations of bromine radical

NBS doesn't produce much Br_2 or HBr so it only replaces benzylic/allylic H's

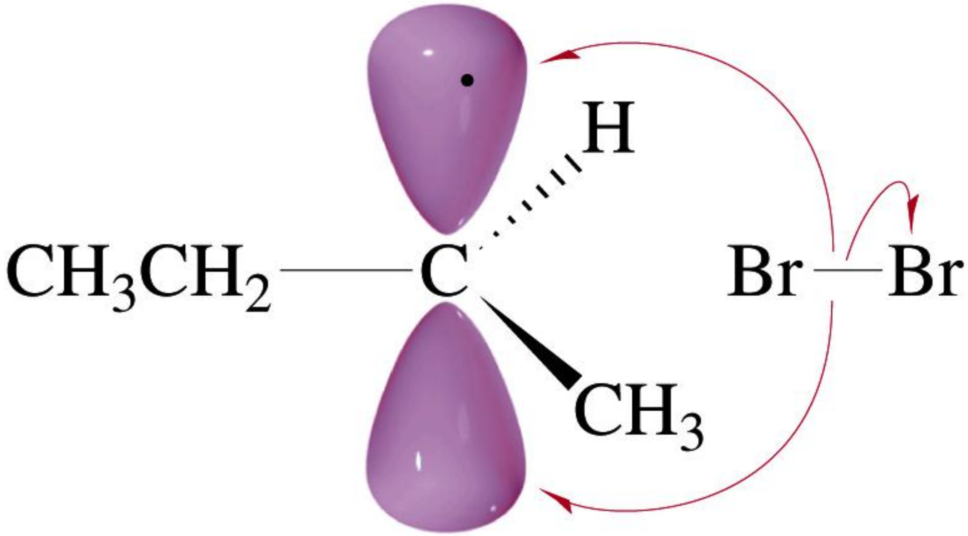


BENZYLIC AND ALLYLIC RADICALS

Allylic or benzylic radical stabilized by resonance. Only H which leads to most stable set of resonance structures is removed (like C+). Unlike C+ case no thermo or kinetic product exists; Br found on all radical-bearing carbons



STEREOCHEMISTRY OF RADICAL SUBSTITUTION



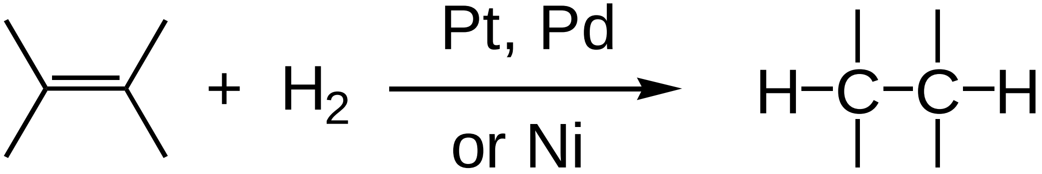
a radical intermediate

Radicals give both enantiomers when they make products like carbocations

ALKENES AND ALKYNES

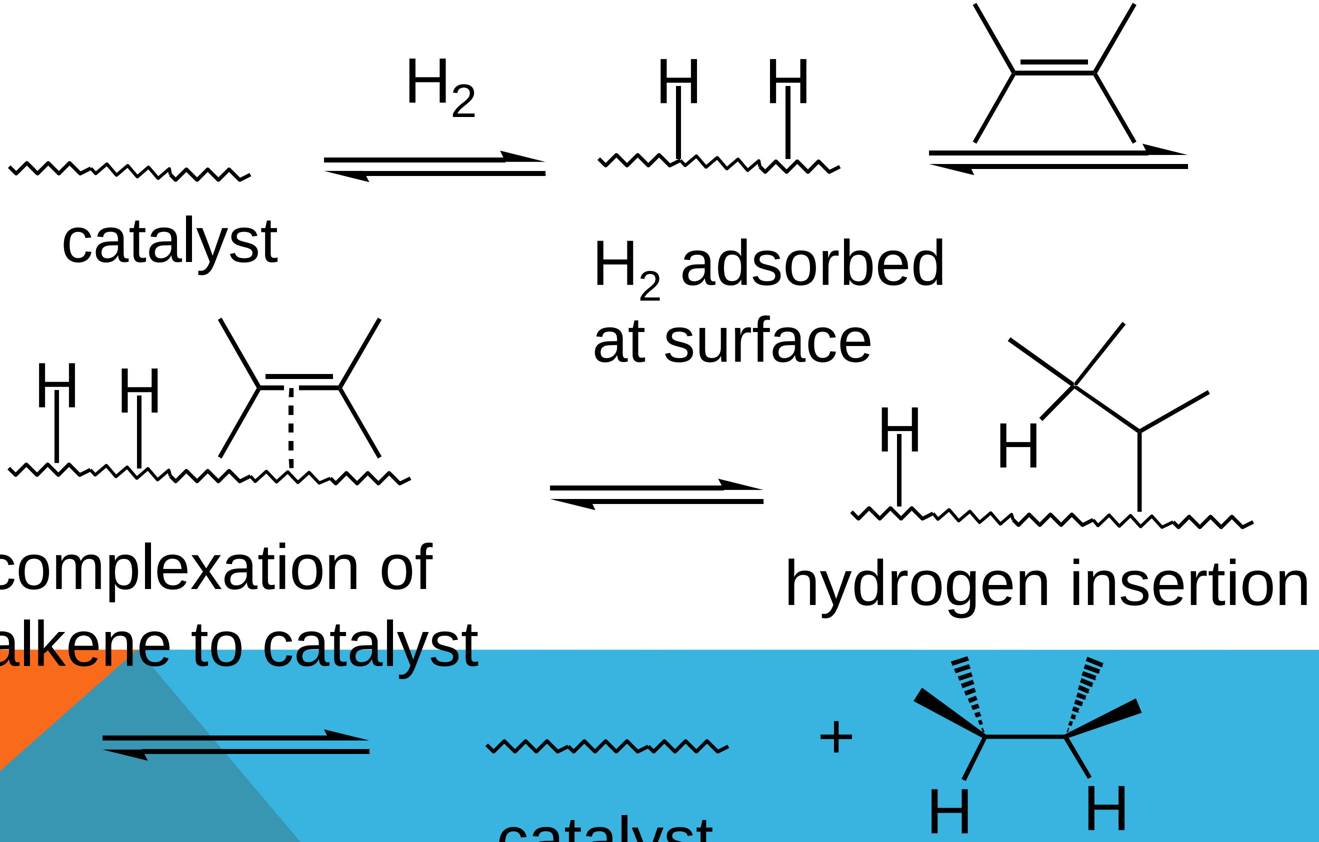
ADDITION REACTIONS

REACTIONS OF ALKENES - CATALYTIC HYDROGENATION



Heat of hydrogenation - the heat liberated during this reaction. ΔH is ~125 kJ/mol for each double bond in the compound.

MECHANISM OF ALKENE HYDROGENATION



catalyst

H_2 adsorbed
at surface

complexation of
alkene to catalyst

hydrogen insertion

catalyst

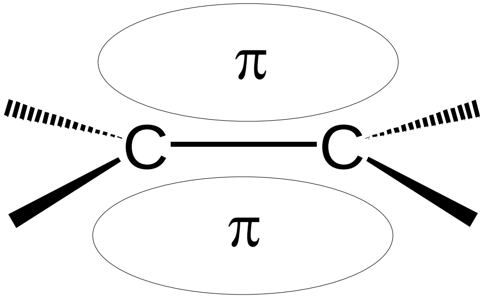
alkane

MECHANISM OF ALKENE HYDROGENATION

Hydrogenation is stereospecific.

The two hydrogens add to the same side of the double bond - a syn addition.

REACTIONS OF ALKENES



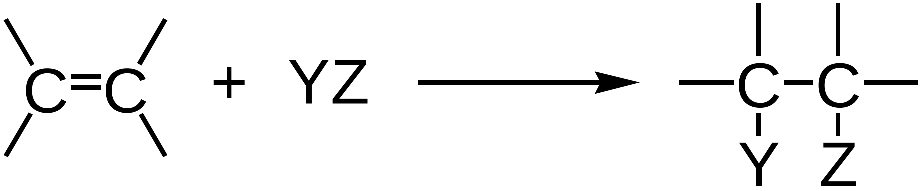
The π electrons are less tightly held than the σ electrons. The double bond therefore acts as a source of electrons - a base – a nucleophile.

It reacts with electron deficient compounds - acids - electrophiles.

ELECTROPHILIC ADDITION

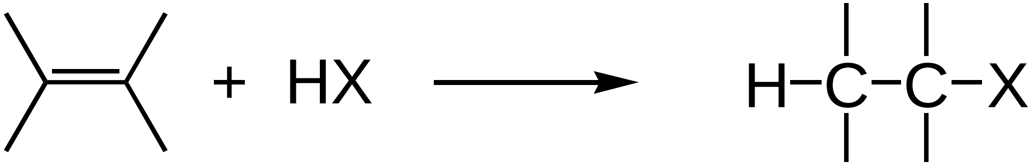
Electron seeking reagents are called electrophilic reagents.

The typical reaction of alkenes is one of electrophilic addition - an acid - base reaction.



Don’t forget that free radicals are electron deficient. They undergo addition reactions with alkenes.

ADDITION OF HYDROGEN HALIDES



HX = HCl, HBr, HI

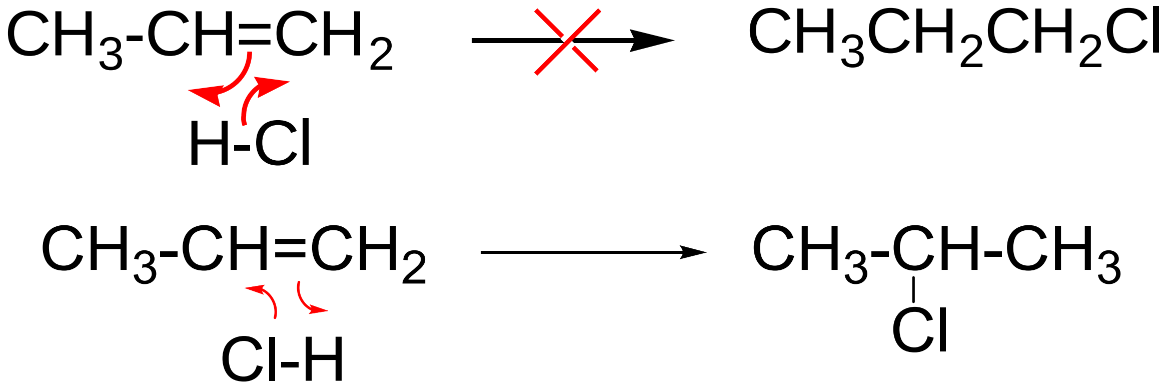
ADDITION OF HYDROGEN HALIDES

$$H_2C{=}CH_2 \;+\; HCl \longrightarrow CH_3CH_2Cl$$

only one product is possible, chloroethane

but....

$$CH_3\text{-}CH{=}CH_2 \longrightarrow ?$$

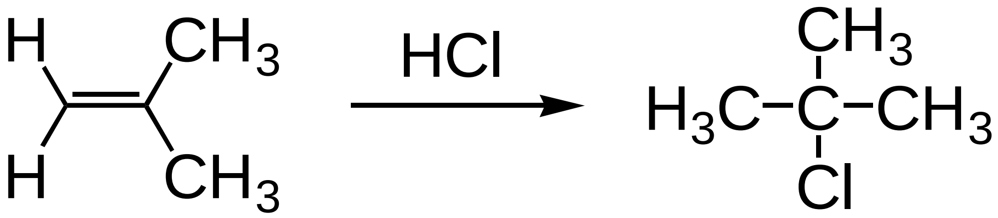


$$CH_3\text{-}CH{=}CH_2 \;\; \text{H-Cl} \;\; \not\longrightarrow CH_3CH_2CH_2Cl$$

$$CH_3\text{-}CH{=}CH_2 \;\; \text{Cl-H} \longrightarrow CH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{C}}H\text{-}CH_3$$

Only 2-chloropropane is formed

MARKOVNIKOV’S RULE



In 1869, Markovnikov proposed that in the addition of an acid to an alkene, the hydrogen of the acid bonds to the carbon which is already bonded to the greater number of hydrogens.

MARKOVNIKOV’S RULE

$$CH_3CH_2CH{=}CHCH_3 + HI \longrightarrow$$

$$CH_3CH_2CHICH_2CH_3 + CH_3CH_2CH_2CHICH_3$$

Each carbon of the double bond is bonded to one H therefore both isomers are formed.

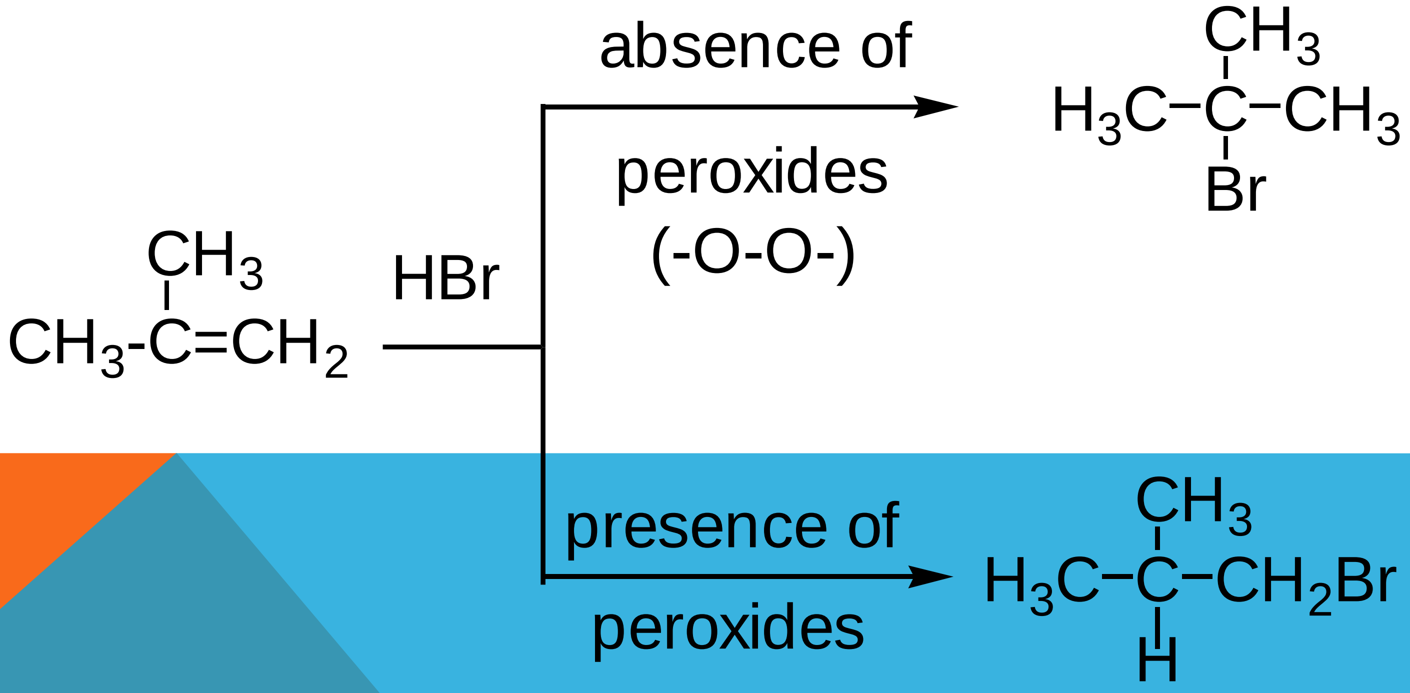
MARKOVNIKOV ADDITION - A REGIOSELECTIVE REACTION

These reactions are said to be **regioselective** because only one of the two possible directions of addition occurs.

Regioselectivity - the preferential formation of one isomer in those situations where a choice is possible.

HBR - THE PEROXIDE EFFECT

1933, Kharasch and Mayo



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

HBr

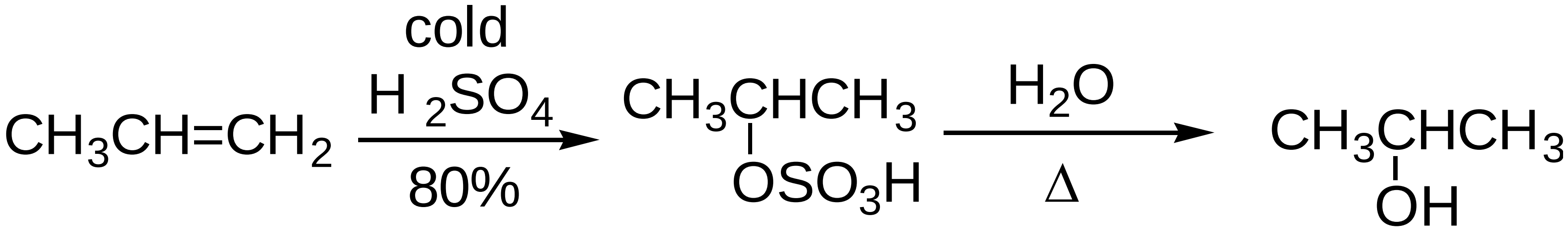
absence of peroxides (-O-O-)

$H_3C-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

presence of peroxides

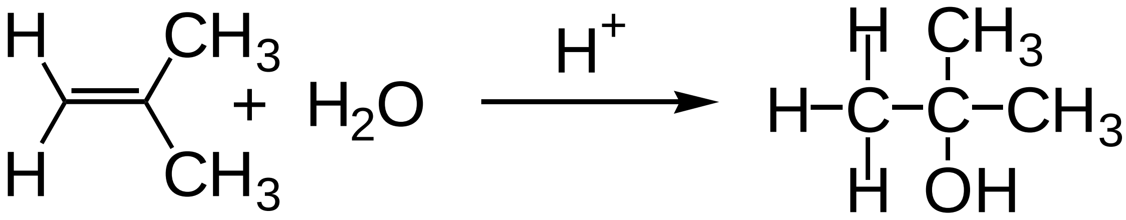
$H_3C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br$

ADDITION OF SULFURIC ACID



$$CH_3CH{=}CH_2 \xrightarrow[80\%]{\text{cold } H_2SO_4} \underset{|\atop OSO_3H}{CH_3CHCH_3} \xrightarrow[\Delta]{H_2O} \underset{|\atop OH}{CH_3CHCH_3}$$

HYDRATION

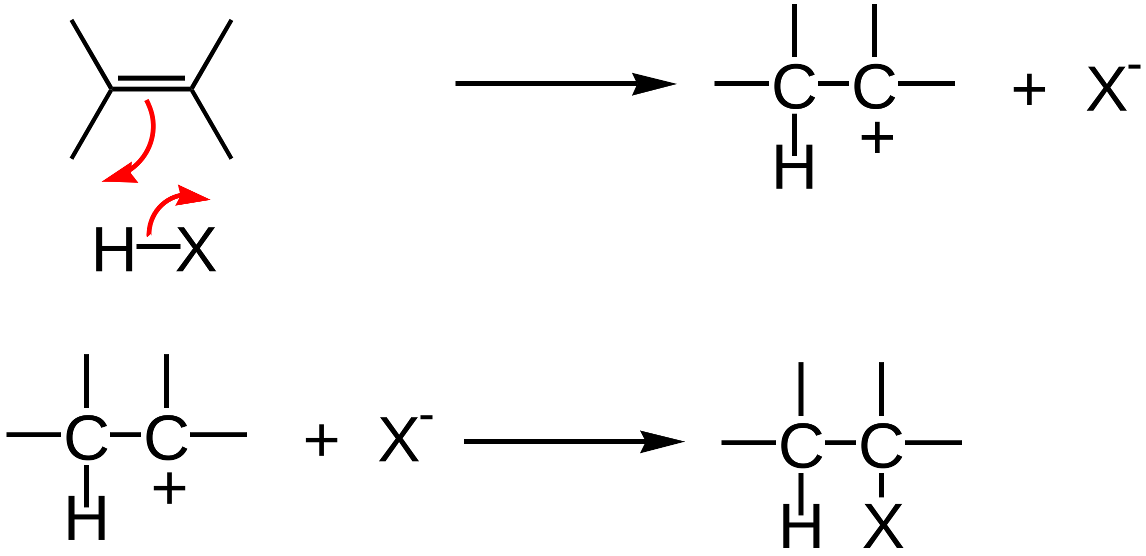


a Markovnikov addition

THE MECHANISM OF THE ADDITION

1.

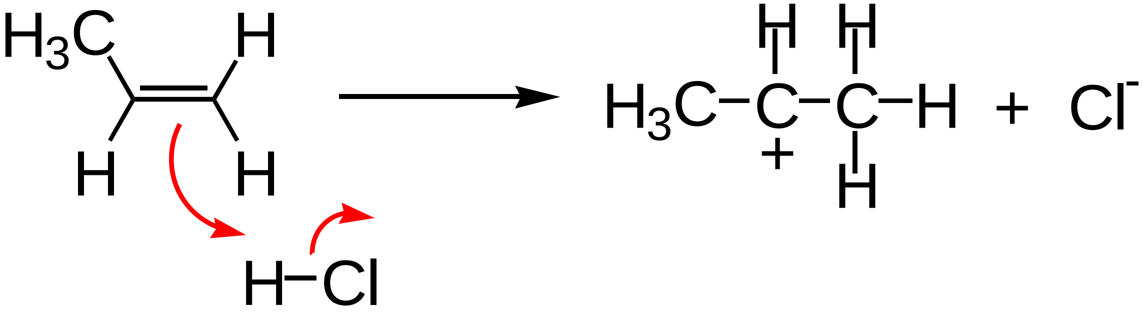
2.



$HX = HCl, HBr, HI, H_2SO_4, H_3O^+$

AN EXAMPLE

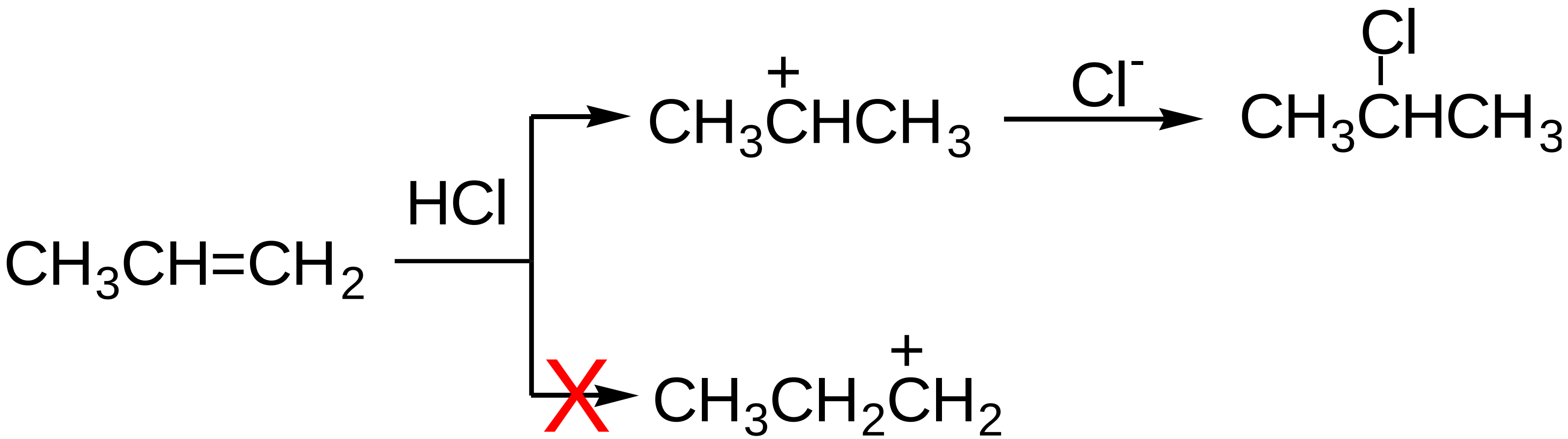
1.



2.

$$H_3C-\underset{+}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H + Cl^- \longrightarrow H_3C-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

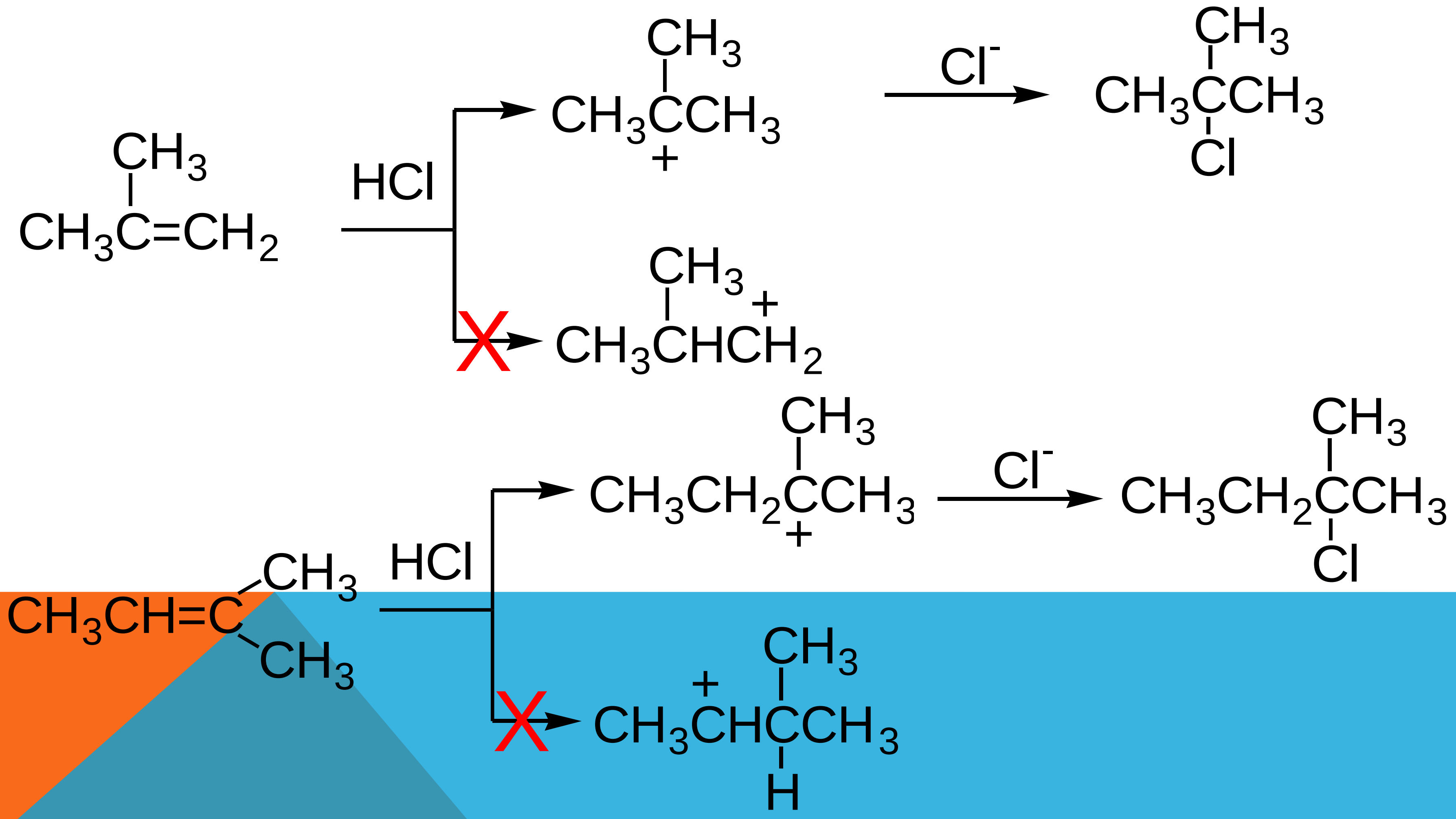
ORIENTATION



$$CH_3CH{=}CH_2 \xrightarrow{HCl} CH_3\overset{+}{C}HCH_3 \xrightarrow{Cl^-} CH_3\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3$$

$$CH_3CH{=}CH_2 \xrightarrow{HCl} \cancel{\longrightarrow} CH_3CH_2\overset{+}{C}H_2$$

ORIENTATION



$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{HCl} CH_3\overset{CH_3}{\underset{+}{C}}CH_3 \xrightarrow{Cl^-} CH_3\overset{CH_3}{\underset{Cl}{C}}CH_3$$

$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{HCl} \cancel{\longrightarrow} CH_3\overset{CH_3}{C}H\overset{+}{C}H_2$$

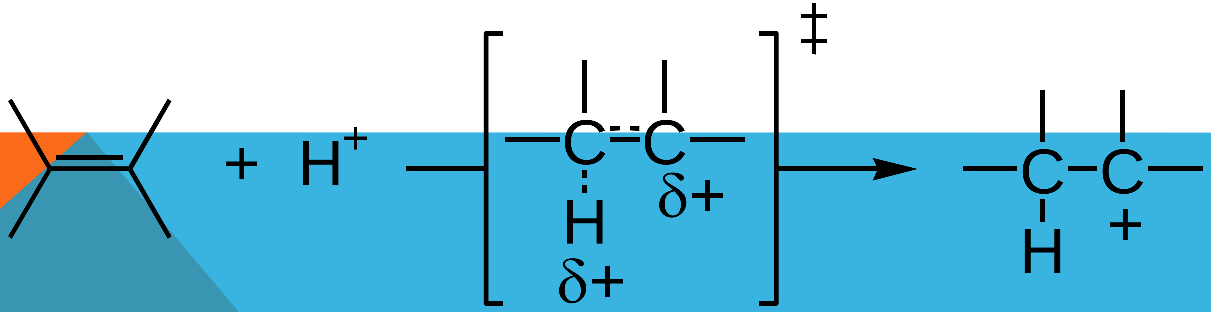
$$CH_3CH=C\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{HCl} CH_3CH_2\overset{CH_3}{\underset{+}{C}}CH_3 \xrightarrow{Cl^-} CH_3CH_2\overset{CH_3}{\underset{Cl}{C}}CH_3$$

$$CH_3CH=C\begin{matrix}CH_3\\CH_3\end{matrix} \xrightarrow{HCl} \cancel{\longrightarrow} CH_3\overset{+}{C}H\overset{CH_3}{\underset{H}{C}}CH_3$$

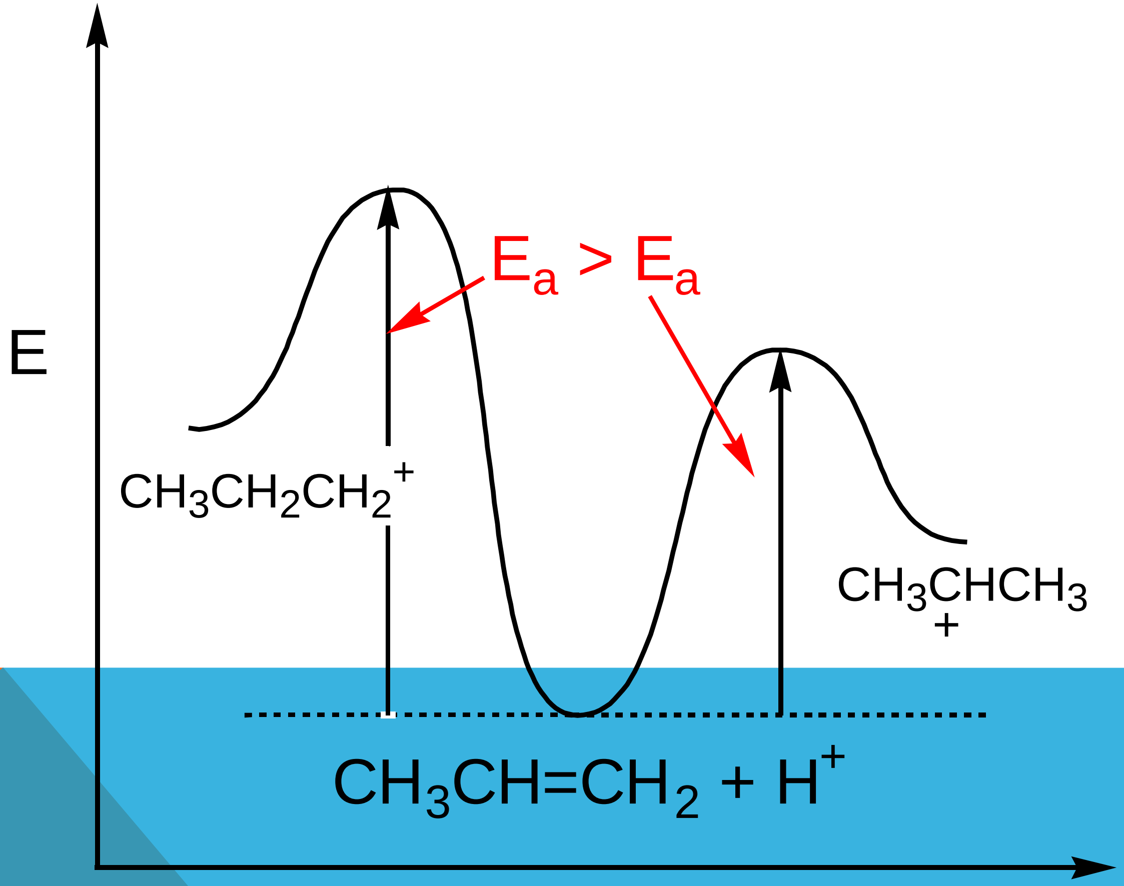
A MORE GENERAL "RULE"

Electrophilic addition to a carbon - carbon double bond involves the intermediate formation of the most stable carbocation.

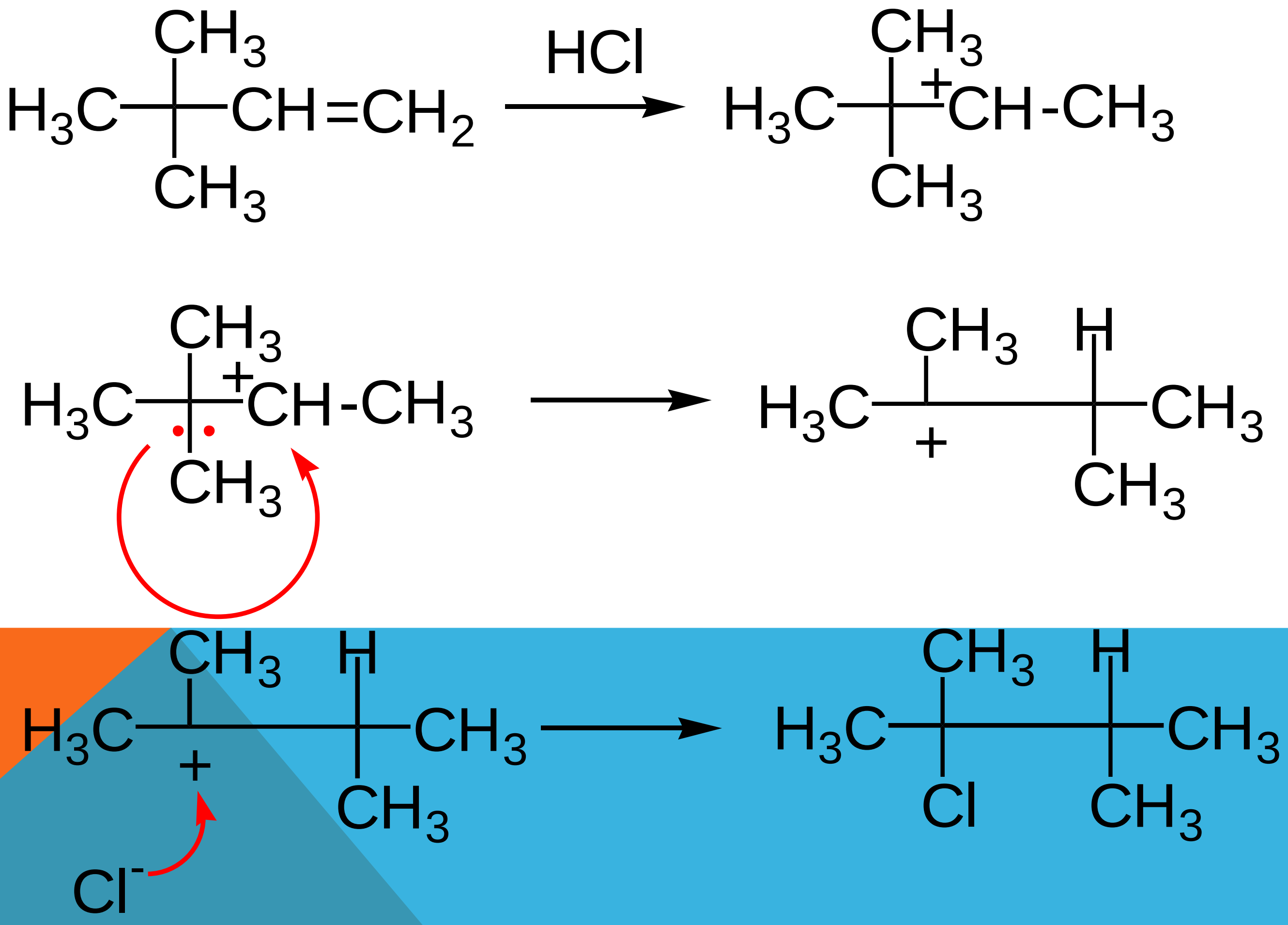
Why? Let's look at the transition state:-



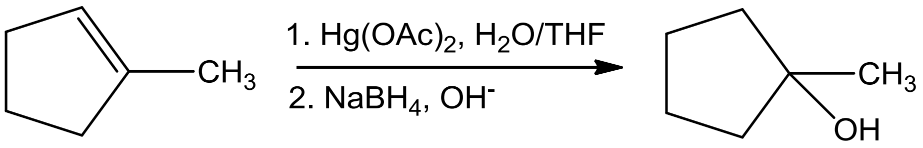
A MORE GENERAL “RULE”



CARBOCATION REARRANGEMENTS



OXYMERCURATION

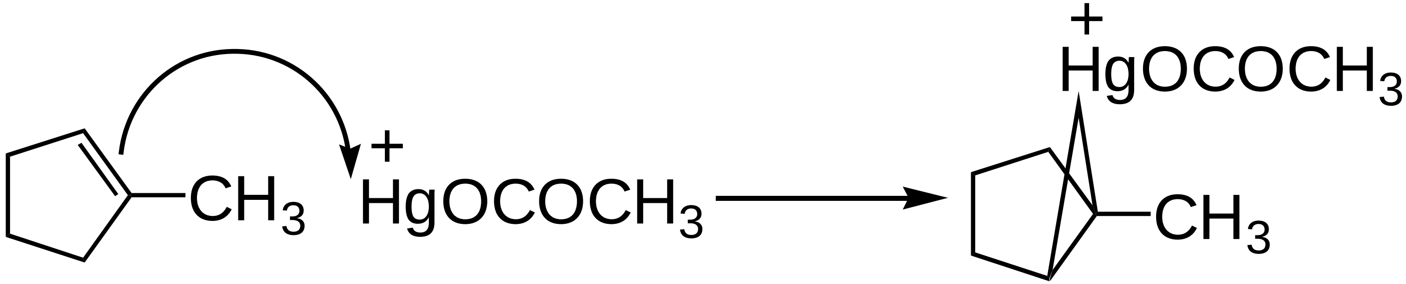


OXYMERCURATION

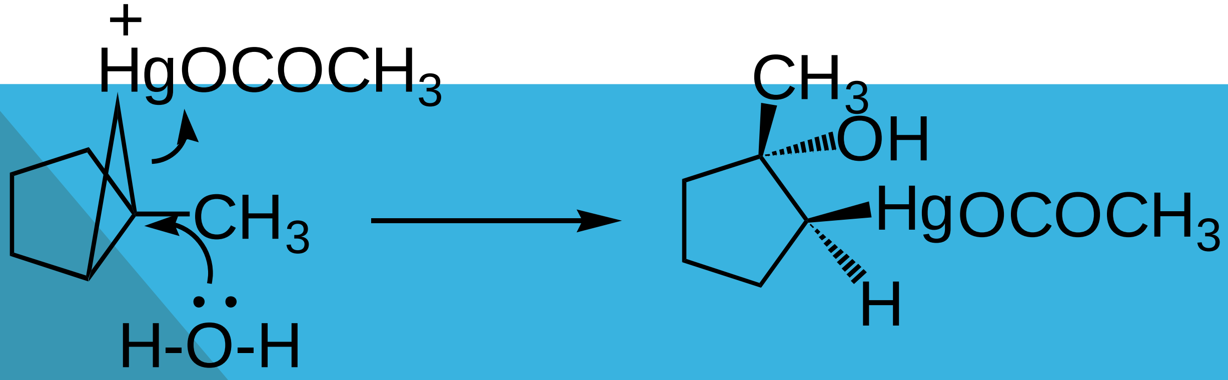
An anti addition via a mercurinium ion:

Dissociation: $Hg(OAc)_2 \rightleftharpoons CH_3CO_2^- + \overset{+}{Hg}OCOCH_3$

Electrophilic attack:

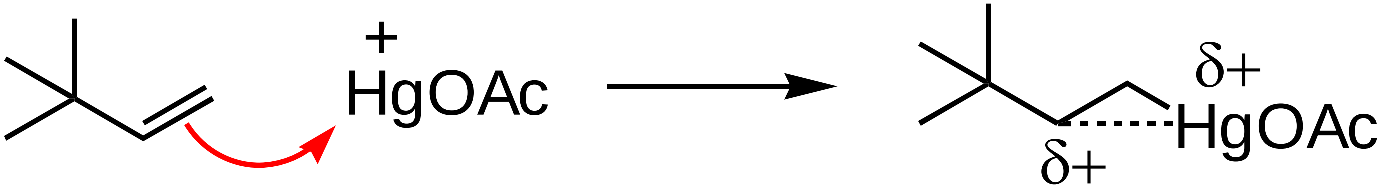


Nucleophilic opening:



OXYMERCURATION

Why do we observe Markovnikov addition?

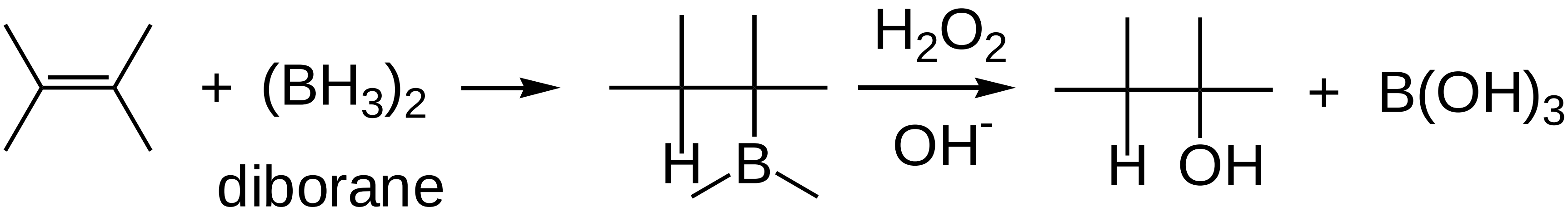


In the mercurinium ion, the positive charge is shared between the more substituted carbon and the mercury atom.

Only a small portion of the charge resides on this carbon but it is sufficient to account for the orientation of the addition but is insufficient to allow a rearrangement to occur.

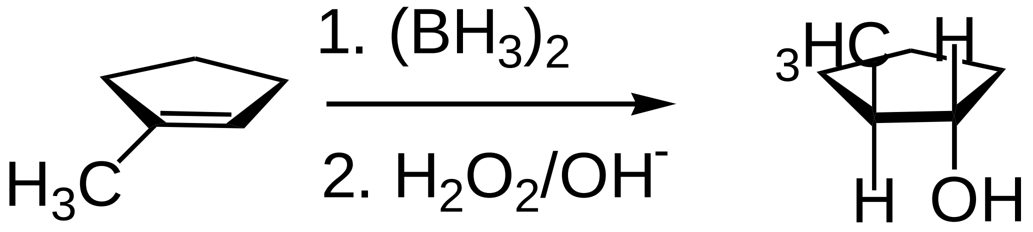
HYDROBORATION

H.C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 83, 2544 (1961)



Brown was co-winner of the 1979 Nobel Prize in Chemistry.

HYDROBORATION



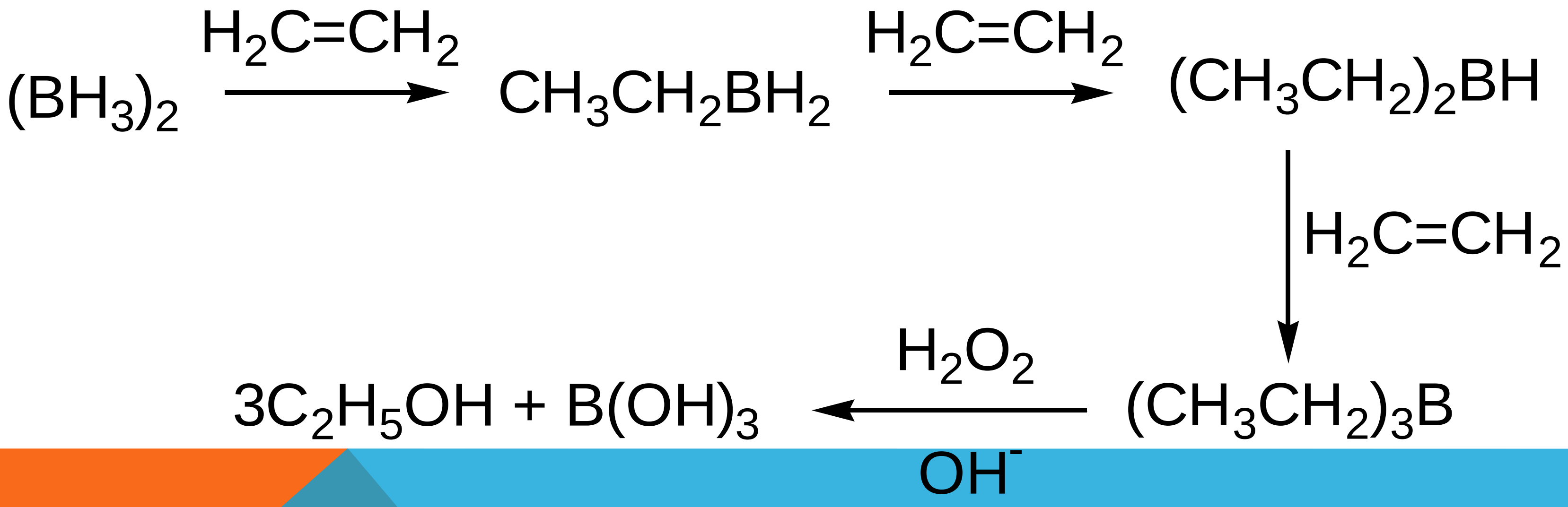
syn
addition

trans-2-methyl-
cyclopentanol

$(CH_3)_3CCH{=}CH_2 \longrightarrow (CH_3)_3CCH_2CH_2OH$

no rearrangement
no carbocation!

HYDROBORATION



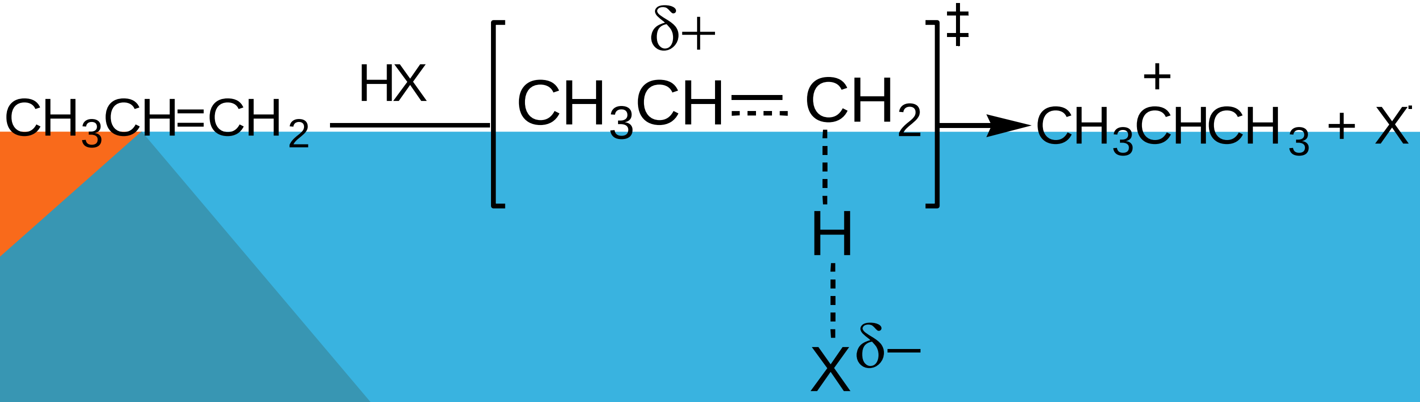
$$(BH_3)_2 \xrightarrow{H_2C{=}CH_2} CH_3CH_2BH_2 \xrightarrow{H_2C{=}CH_2} (CH_3CH_2)_2BH$$

$$(CH_3CH_2)_2BH \xrightarrow{H_2C{=}CH_2} (CH_3CH_2)_3B$$

$$(CH_3CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3C_2H_5OH + B(OH)_3$$

HYDROBORATION - THE MECHANISM

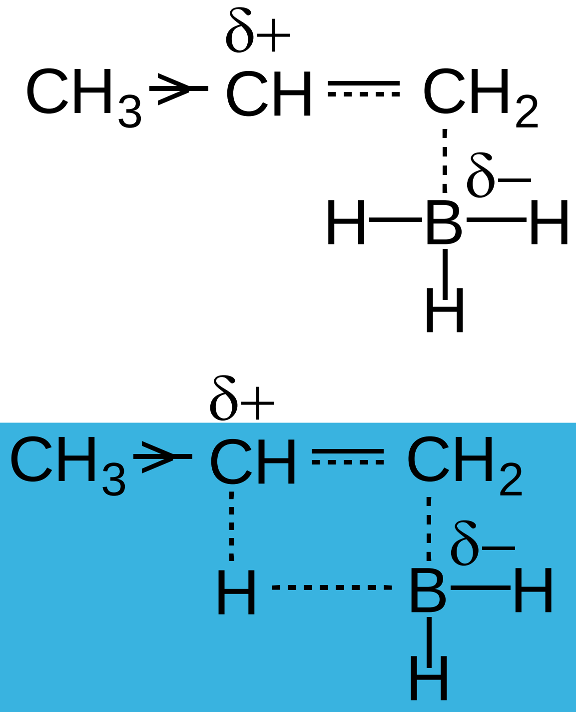
$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ (BH_3)_2} CH_3CH_2CH_2OH$$



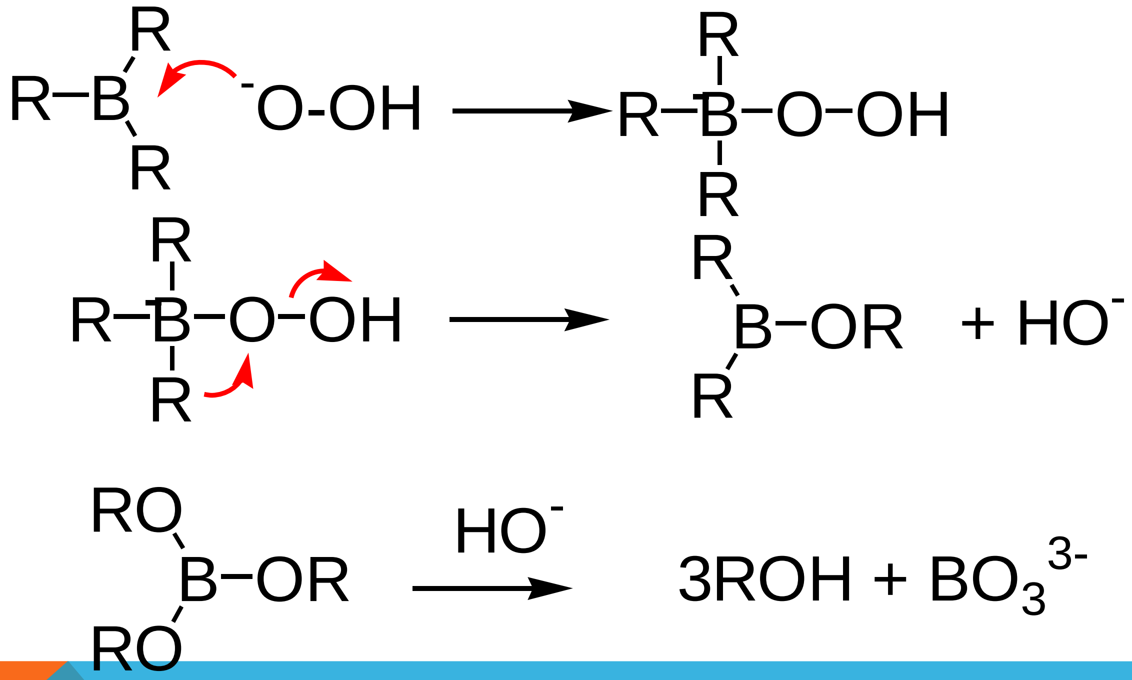
$$CH_3CH{=}CH_2 \xrightarrow{HX} \left[CH_3\overset{\delta+}{CH}{=}\underset{\substack{\vdots\\ H\\ \vdots\\ X^{\delta-}}}{CH_2} \right]^{\ddagger} \longrightarrow CH_3\overset{+}{C}HCH_3 + X^-$$

HYDROBORATION - THE MECHANISM

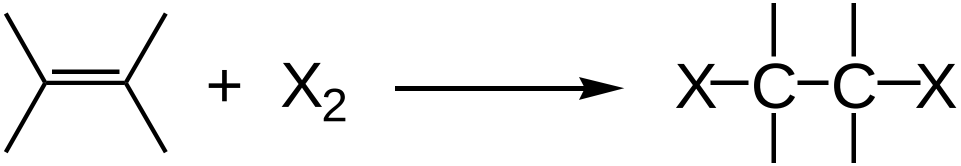
$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ (BH_3)_2} CH_3CH_2CH_2OH$$



HYDROBORATION - THE MECHANISM



ADDITION OF HALOGENS



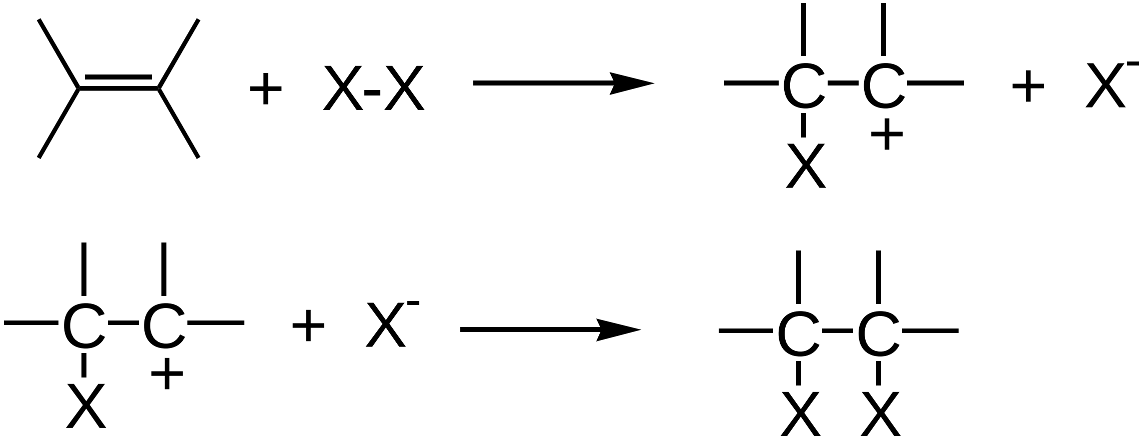
X_2 = Cl_2, Br_2

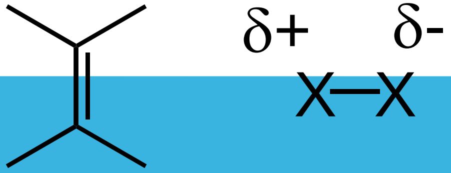
usually iodine does not react

$$CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2\ \text{in}} CH_3CHBrCH_2Br$$

1,2-dibromopropane

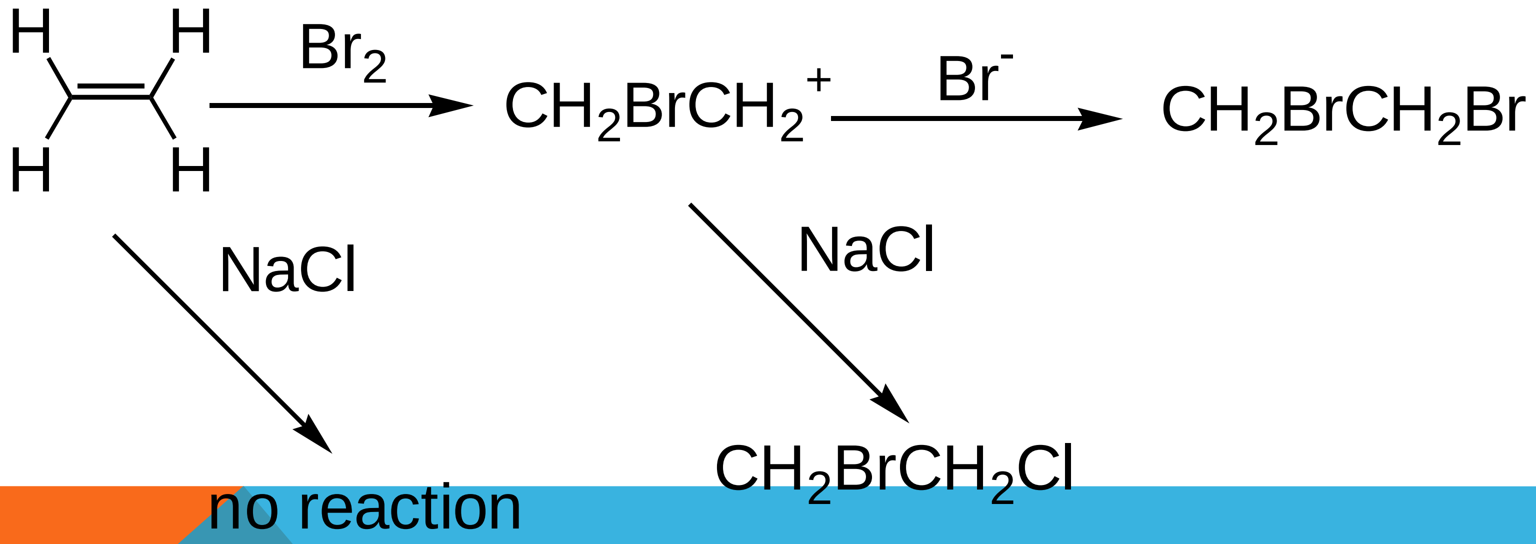
MECHANISM OF X_2 ADDITION





polarisation

MECHANISM OF X_2 ADDITION



$$\xrightarrow{Br_2} CH_2BrCH_2^+ \xrightarrow{Br^-} CH_2BrCH_2Br$$

NaCl

no reaction

NaCl

CH_2BrCH_2Cl

STEREOSPECIFIC REACTIONS

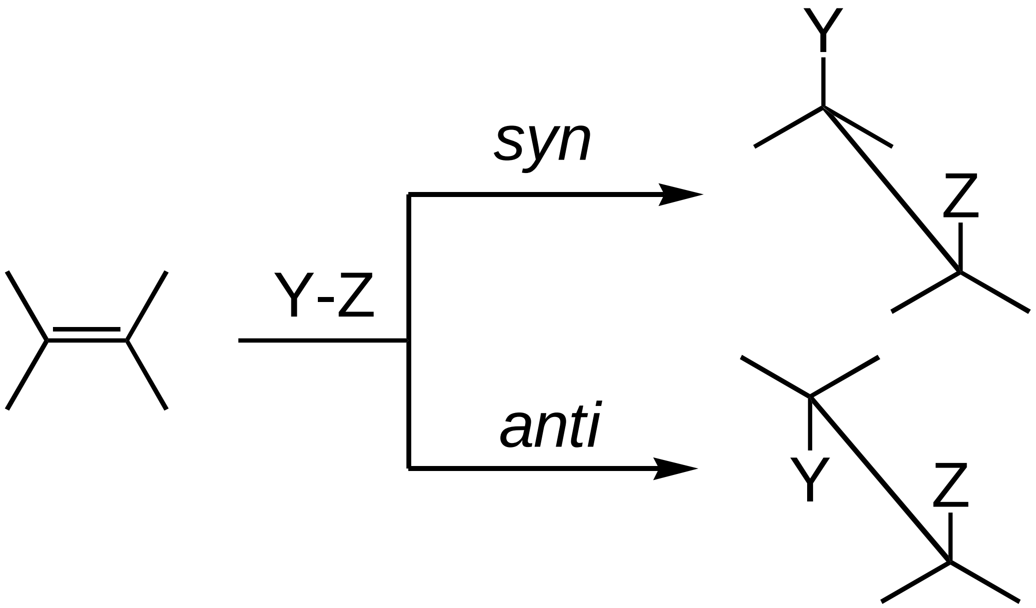
$$CH_3CH{=}CHCH_3 \xrightarrow{Br_2} CH_3\overset{*}{C}HBr\overset{*}{C}HBrCH_3$$

(Z)-2-butene gives racemic 2,3-dibromobutane and no meso compound is formed.

(E)-2-butene gives only meso-2,3-dibromobutane.

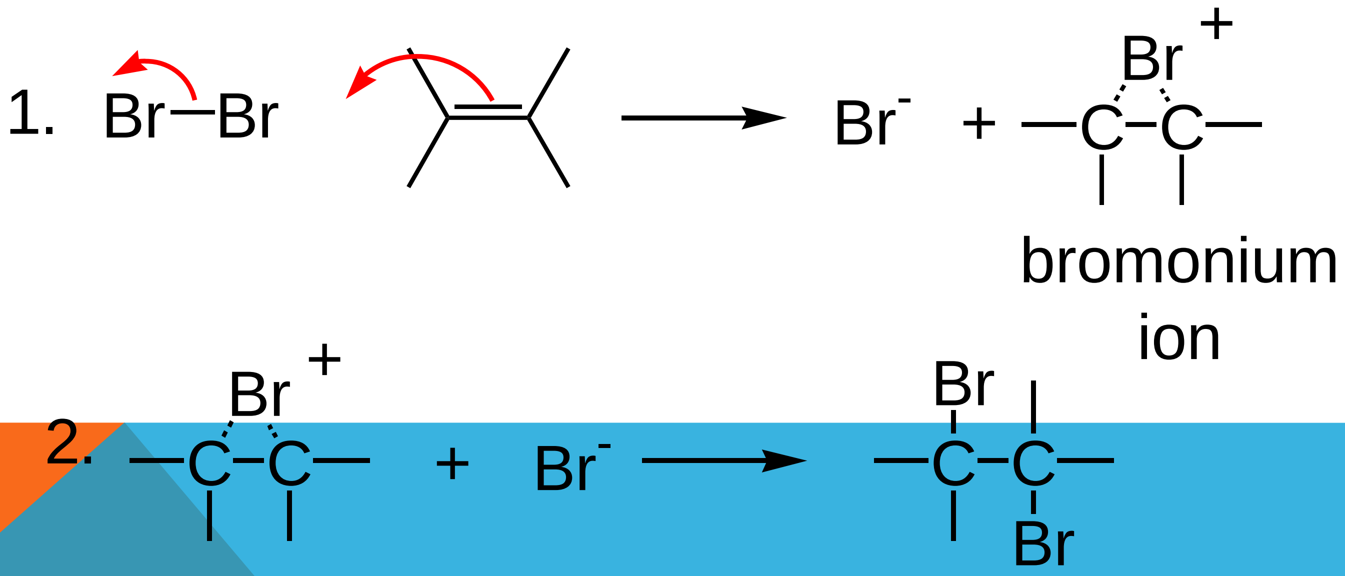
A reaction is stereospecific if a particular stereoisomer of the reactant produces a specific stereoisomer of the product.

SYN AND *ANTI* ADDITION



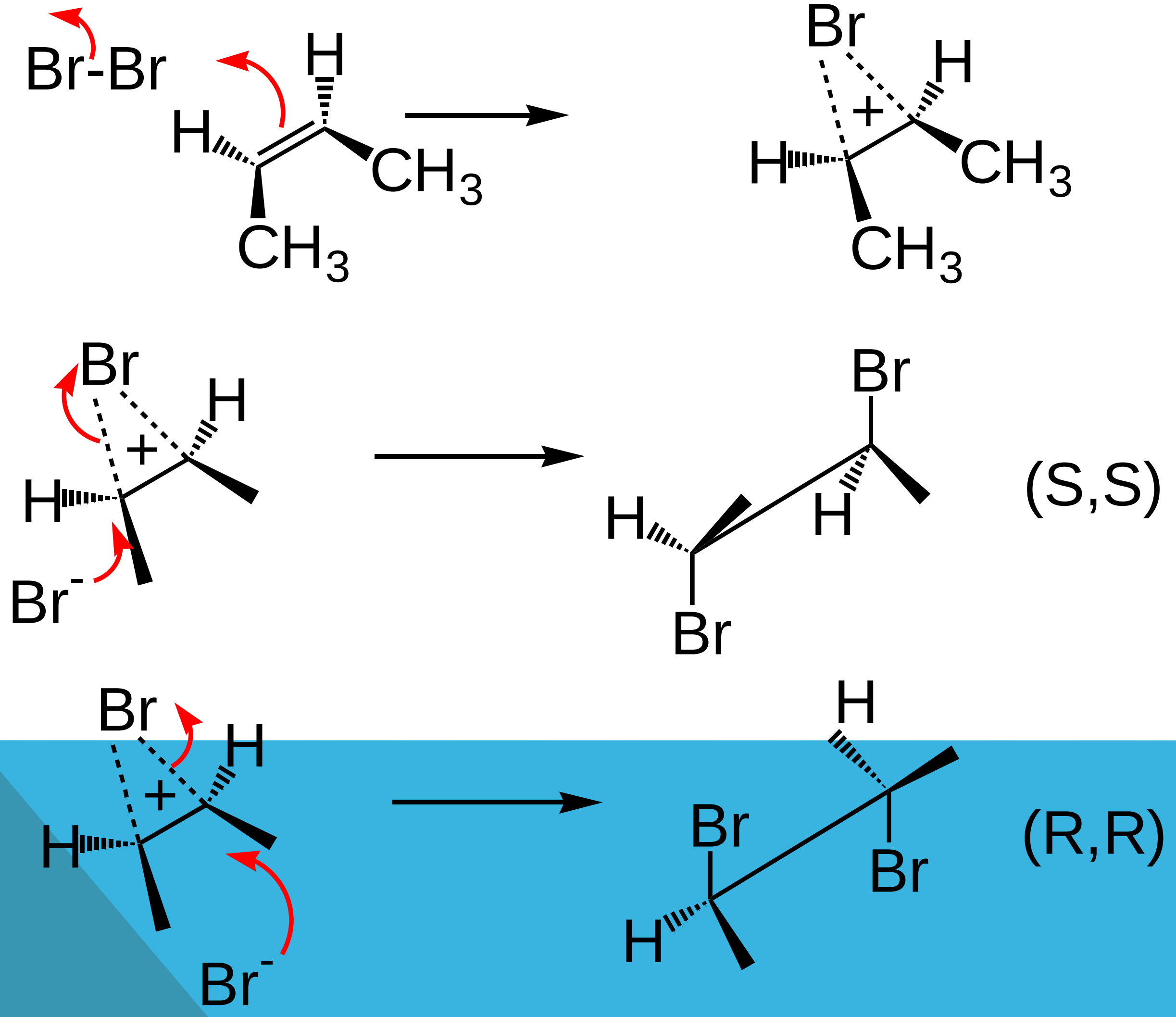
BROMINE ADDITION - AN *ANTI* ADDITION

I. Roberts and G.E. Kimball, *J. Am. Chem. Soc.*, 59, 947 (1937)

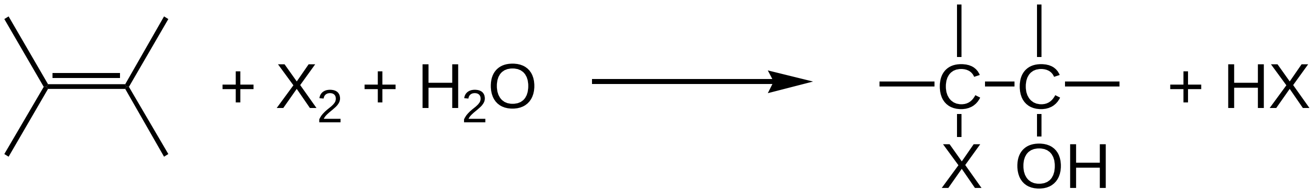


bromonium ion

THE BROMONIUM ION

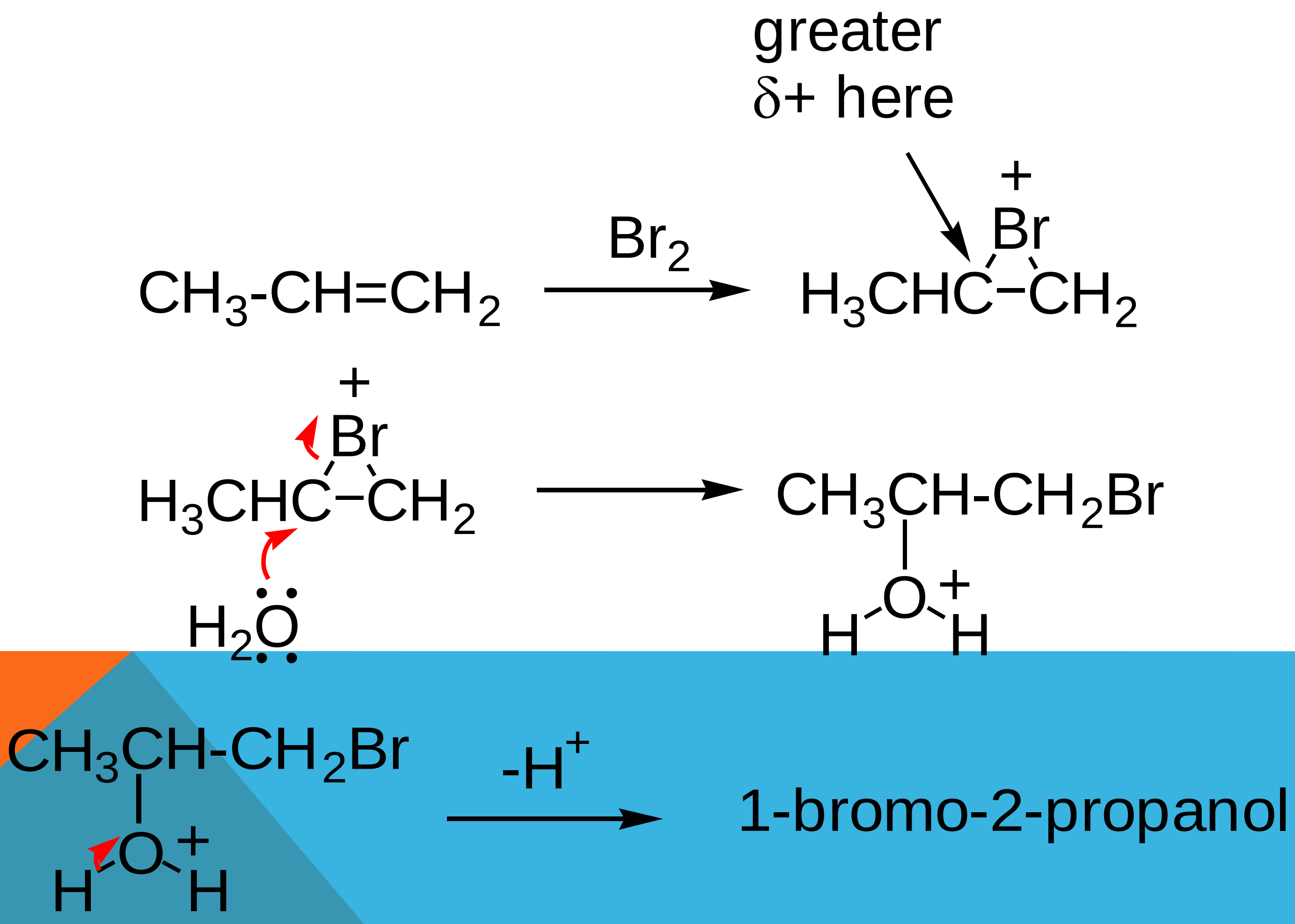


HALOHYDRIN FORMATION



$X_2 = Cl_2, Br_2$

HALOHYDRIN FORMATION



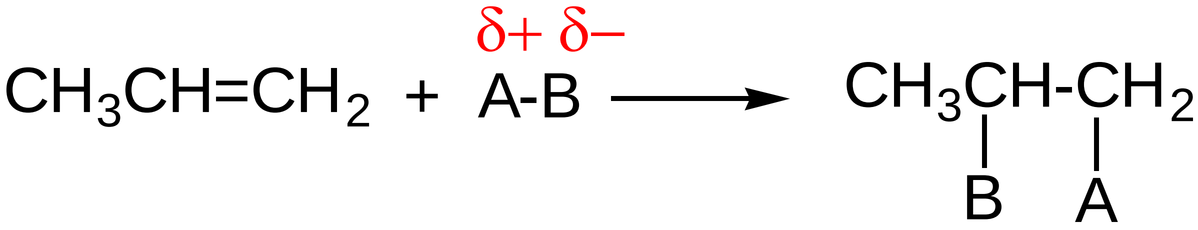
$CH_3\text{-}CH{=}CH_2 \xrightarrow{Br_2}$

greater
δ+ here

$\xrightarrow{-H^+}$ 1-bromo-2-propanol

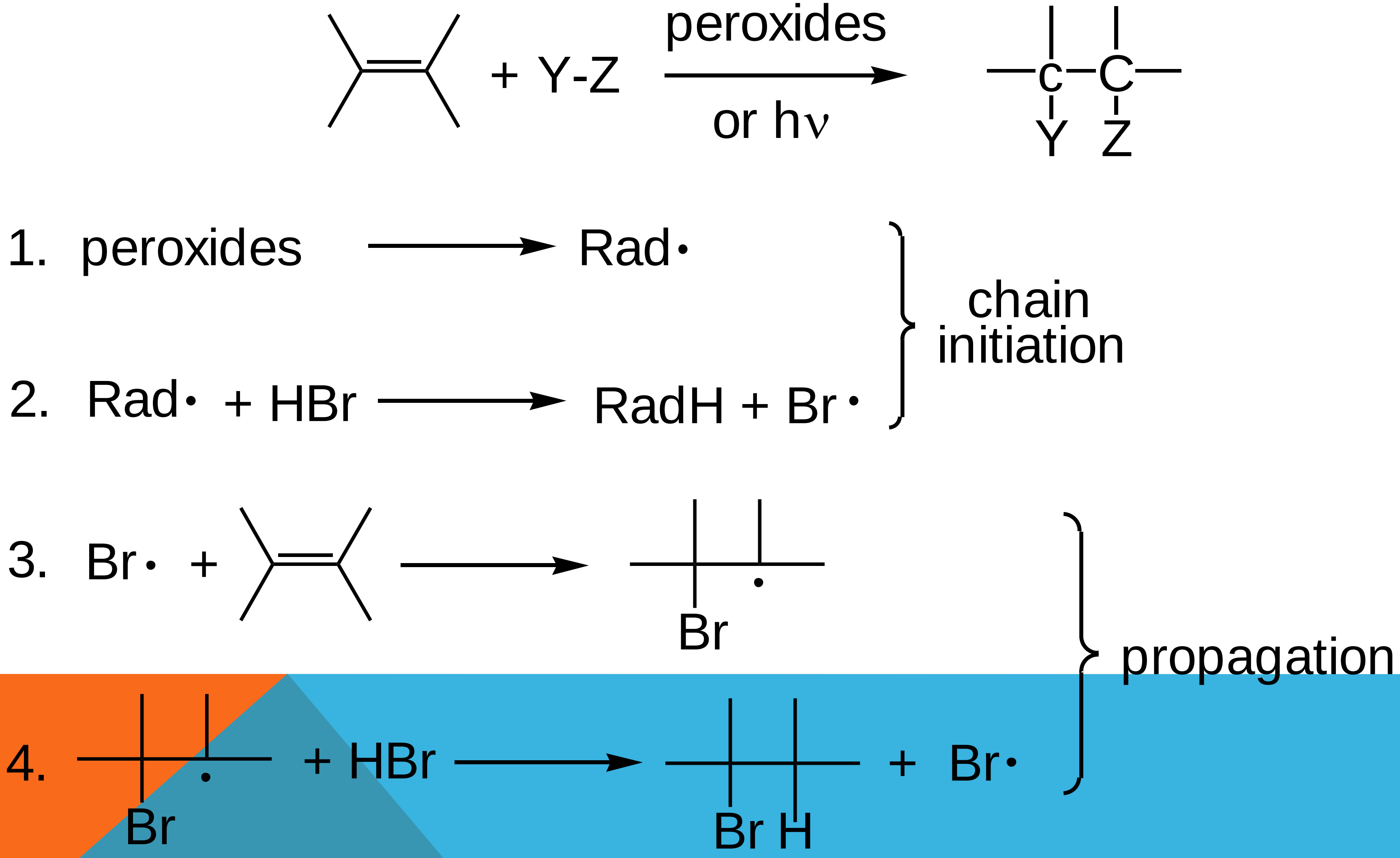
UNSYMMETRIC ELECTROPHILES

In the electrophilic addition of an unsymmetric reagent, the electrophilic part adds to the less substituted carbon of the alkene unit:



$$CH_3CH{=}CH_2 + \overset{\delta+}{A}\text{-}\overset{\delta-}{B} \longrightarrow CH_3\underset{B}{\underset{|}{CH}}\text{-}\underset{A}{\underset{|}{CH_2}}$$

FREE RADICAL ADDITION REACTIONS



1. peroxides $\longrightarrow$ Rad•
2. Rad• + HBr $\longrightarrow$ RadH + Br•

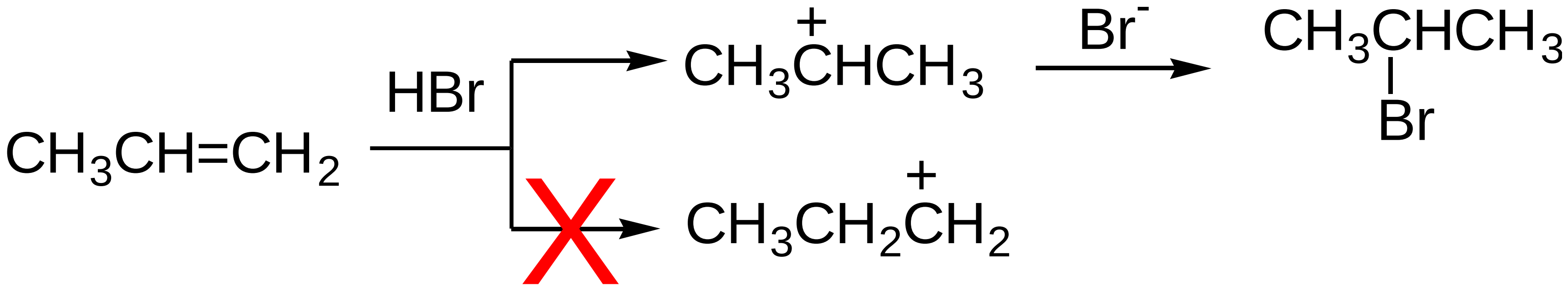
chain initiation

3. Br• +

4. + HBr $\longrightarrow$ + Br•

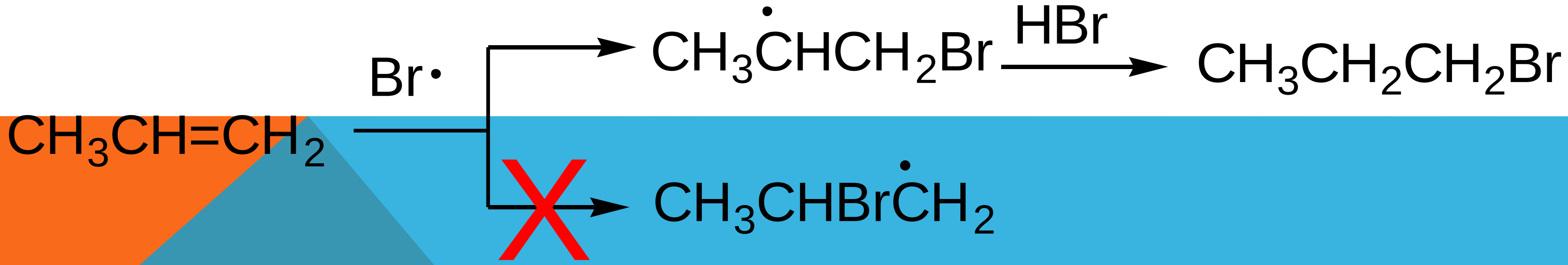
propagation

IONIC VS RADICAL ADDITION



$CH_3CH=CH_2 \xrightarrow{HBr} CH_3\overset{+}{C}HCH_3 \xrightarrow{Br^-} CH_3\underset{Br}{C}HCH_3$

$CH_3CH=CH_2 \xrightarrow{HBr} \cancel{\longrightarrow} CH_3CH_2\overset{+}{C}H_2$



$CH_3CH=CH_2 \xrightarrow{Br\cdot} CH_3\dot{C}HCH_2Br \xrightarrow{HBr} CH_3CH_2CH_2Br$

$CH_3CH=CH_2 \xrightarrow{Br\cdot} \cancel{\longrightarrow} CH_3CHBr\dot{C}H_2$

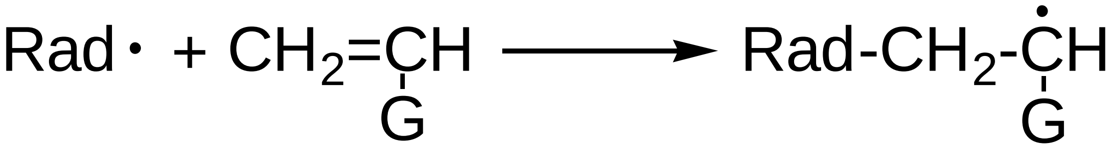
POLYMERIZATION

A polymer is a long chain molecule made up of structural units (monomers) joined together.

FREE RADICAL POLYMERIZATION OF ALKENES

Initiation

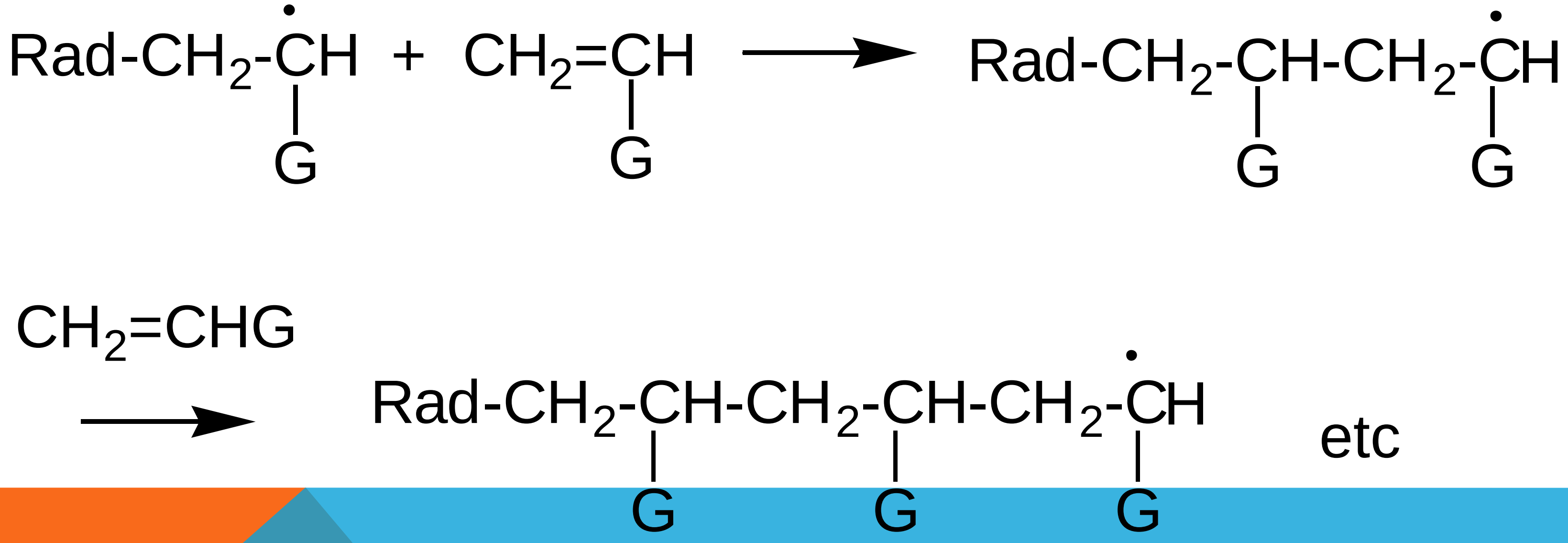
$$\text{peroxide} \longrightarrow \mathrm{Rad}\cdot$$



$$\mathrm{Rad}\cdot + \mathrm{CH_2{=}}\underset{\mathrm{G}}{\underset{|}{\mathrm{C}}}\mathrm{H} \longrightarrow \mathrm{Rad{-}CH_2{-}}\underset{\mathrm{G}}{\underset{|}{\overset{\bullet}{\mathrm{C}}}}\mathrm{H}$$

FREE RADICAL POLYMERIZATION OF ALKENES

chain propagation



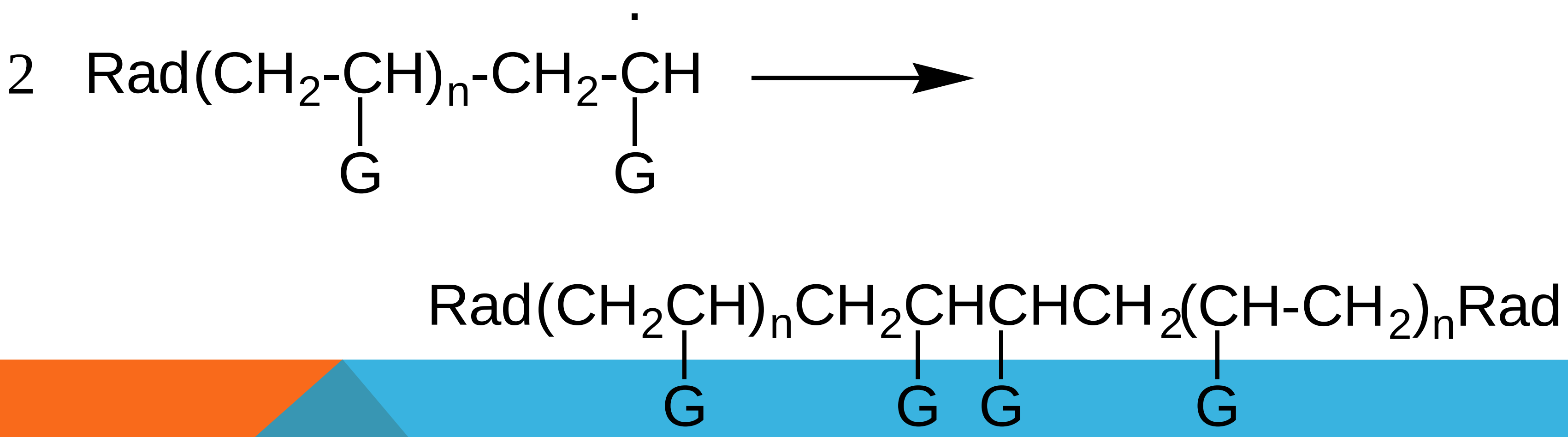
$$\mathrm{Rad\text{-}CH_2\text{-}}\underset{\underset{G}{|}}{\overset{\bullet}{\mathrm{C}}}\mathrm{H} + \mathrm{CH_2{=}}\underset{\underset{G}{|}}{\mathrm{C}}\mathrm{H} \longrightarrow \mathrm{Rad\text{-}CH_2\text{-}}\underset{\underset{G}{|}}{\mathrm{C}}\mathrm{H\text{-}CH_2\text{-}}\underset{\underset{G}{|}}{\overset{\bullet}{\mathrm{C}}}\mathrm{H}$$

$$\xrightarrow{\mathrm{CH_2{=}CHG}} \mathrm{Rad\text{-}CH_2\text{-}}\underset{\underset{G}{|}}{\mathrm{C}}\mathrm{H\text{-}CH_2\text{-}}\underset{\underset{G}{|}}{\mathrm{C}}\mathrm{H\text{-}CH_2\text{-}}\underset{\underset{G}{|}}{\overset{\bullet}{\mathrm{C}}}\mathrm{H} \quad \text{etc}$$

FREE RADICAL POLYMERIZATION OF ALKENES

Chain termination

combination

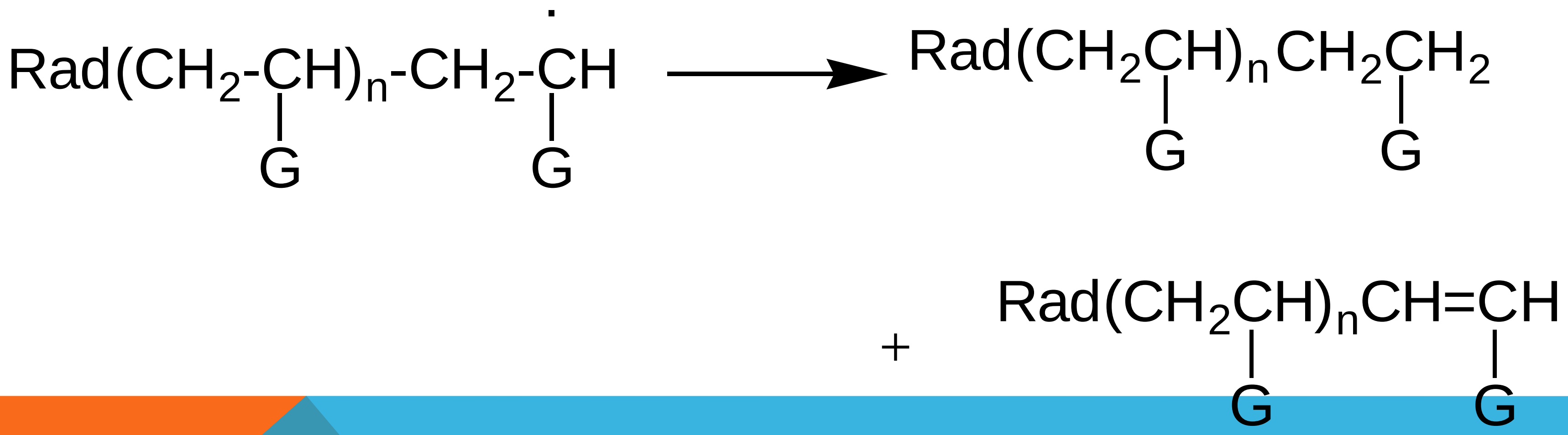


$$2\ \mathrm{Rad(CH_2}\text{-}\underset{\mathrm{G}}{\underset{|}{\mathrm{CH}}}\mathrm{)_n}\text{-}\mathrm{CH_2}\text{-}\underset{\mathrm{G}}{\underset{|}{\overset{\cdot}{\mathrm{CH}}}} \longrightarrow \mathrm{Rad(CH_2}\underset{\mathrm{G}}{\underset{|}{\mathrm{CH}}}\mathrm{)_nCH_2}\underset{\mathrm{G}}{\underset{|}{\mathrm{CH}}}\underset{\mathrm{G}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_2(}\underset{\mathrm{G}}{\underset{|}{\mathrm{CH}}}\text{-}\mathrm{CH_2)_nRad}$$

FREE RADICAL POLYMERIZATION OF ALKENES

Chain termination

disproportionation



$$\mathrm{Rad(CH_2\text{-}\underset{G}{CH})_n\text{-}CH_2\text{-}\underset{G}{\dot{C}H}} \longrightarrow \mathrm{Rad(CH_2\underset{G}{CH})_n\,CH_2\underset{G}{CH_2}} + \mathrm{Rad(CH_2\underset{G}{CH})_n\underset{G}{CH}{=}\underset{G}{CH}}$$

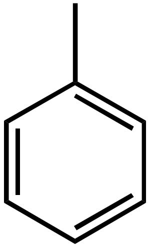
EXAMPLES

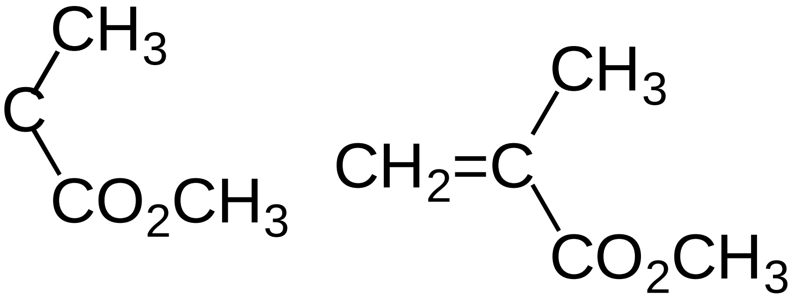
G	monomer	polymer
Cl	$CH_2=CHCl$	$-CH_2CHCl-CH_2CHCl-CH_2-$
	vinyl chloride	polyvinyl chloride, PVC
CN	$CH_2=CHCN$	$-CH_2CHCN-CH_2CHCN-$
	acrylonitrile	polyacrylonitrile
		Orlon, Acrilon

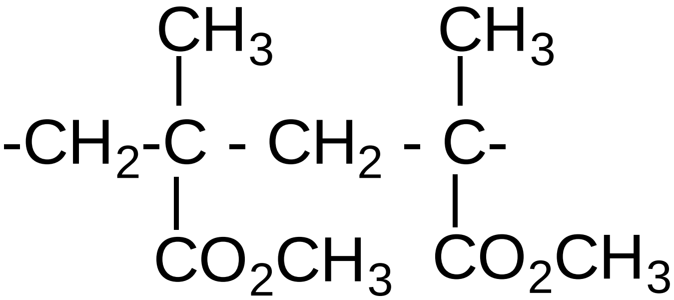
EXAMPLES

G	monomer	polymer
Ph	CH_2=CHPh styrene	-CH_2CHPh-CH_2CHPh- polystyrene

Ph =







$$-CH_2-\underset{\displaystyle CO_2CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2 - \underset{\displaystyle CO_2CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-$$

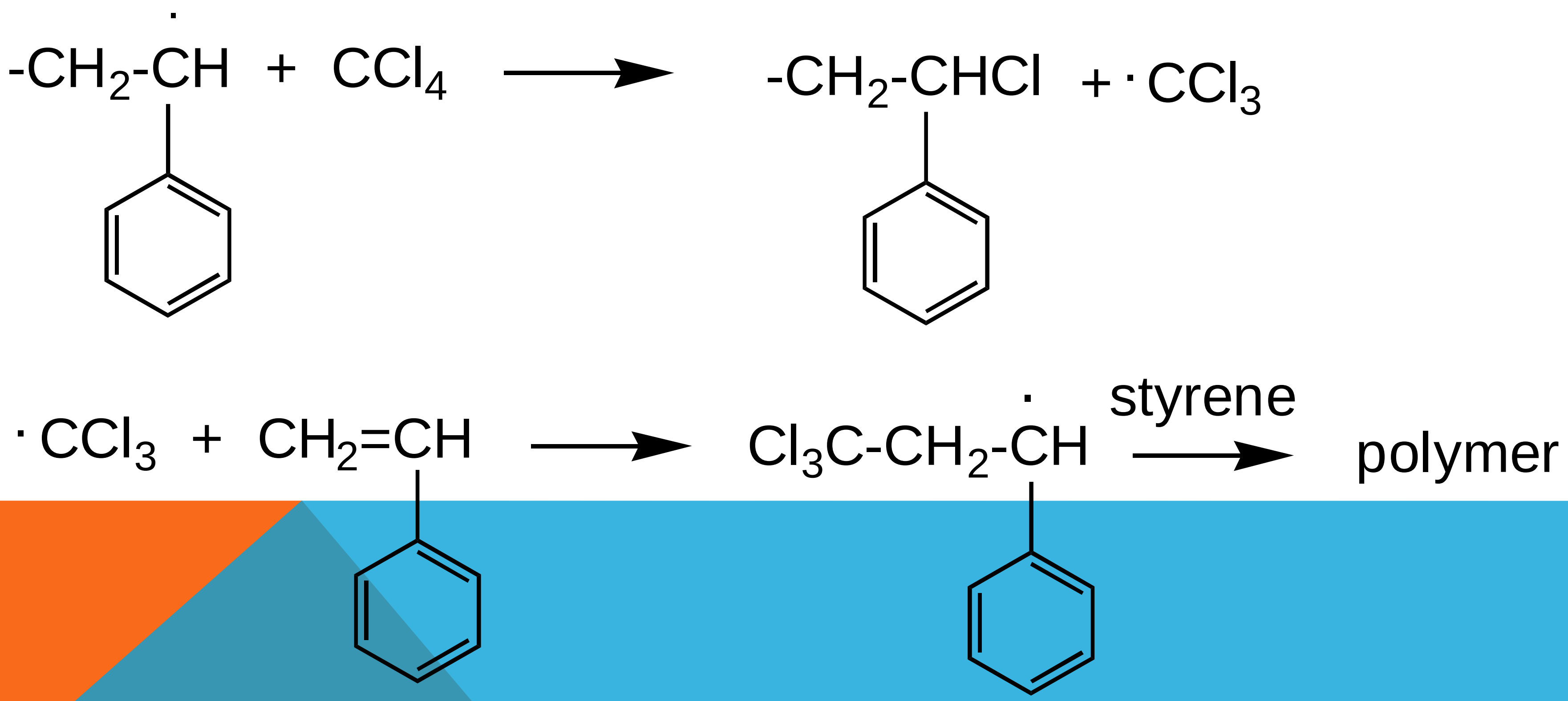
methyl methacrylate

poly(methyl methacrylate)

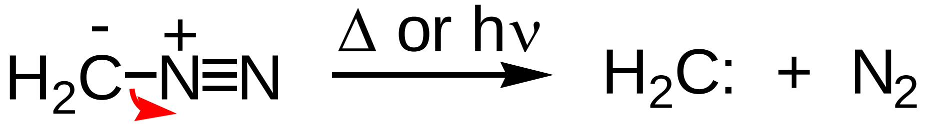
Plexiglas, Lucite

POLYMERIZATION

The addition of other compounds can modify the polymerization:



CARBENES



$$H_2\overset{-}{C}-\overset{+}{N}\equiv N \xrightarrow{\Delta \text{ or } h\nu} H_2C: \; + \; N_2$$

diazomethane

methylene

$$RO^- \, K^+ + H\text{-}CCl_3 \longrightarrow ROH + K^+ + Cl^- + Cl_2C:$$

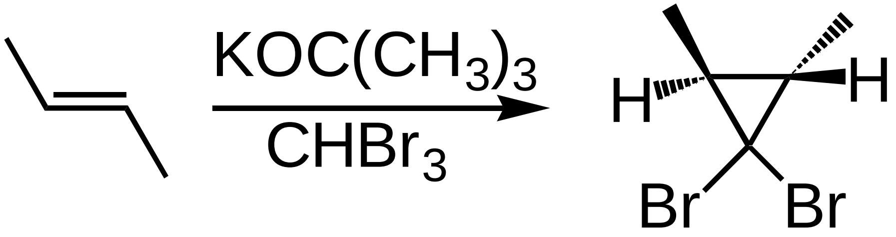
dichlorocarbene

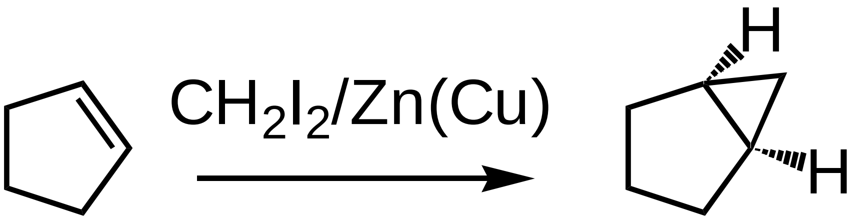
$$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2ZnI$$

a carbenoid

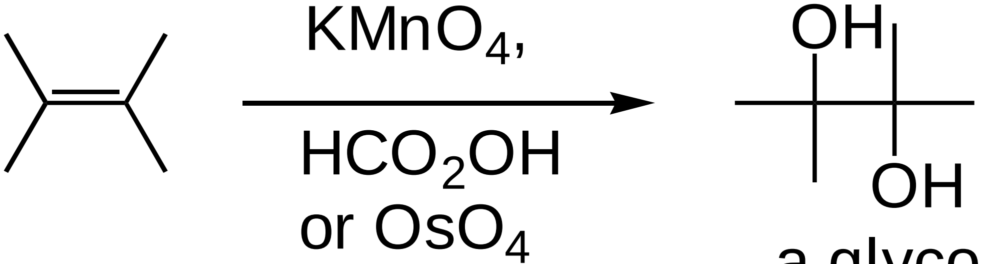
Carbenes (and carbenoids) add to alkenes in a stereospecific manner to form cyclopropanes.

CARBENES





HYDROXYLATION



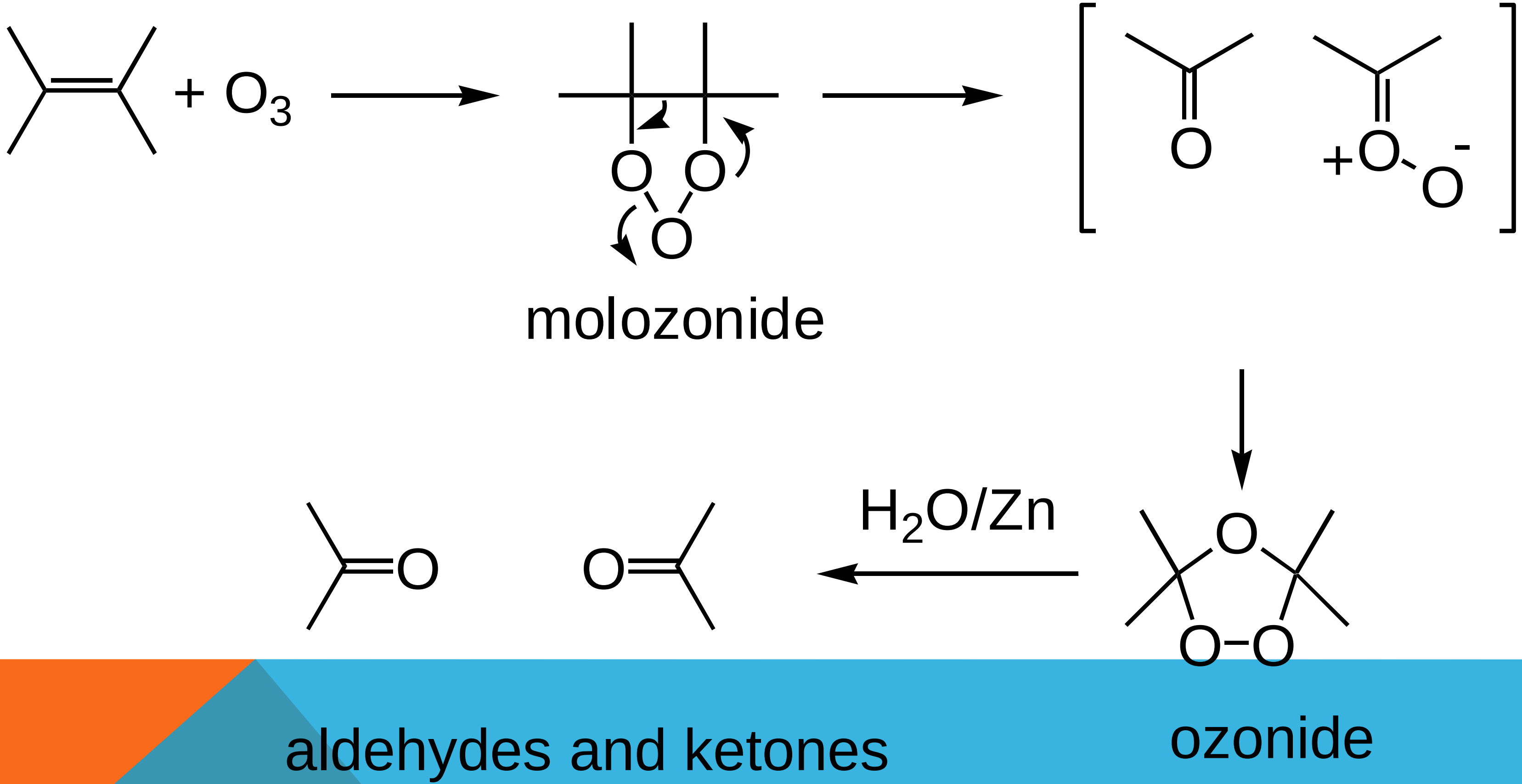
$KMnO_4$,

HCO_2OH

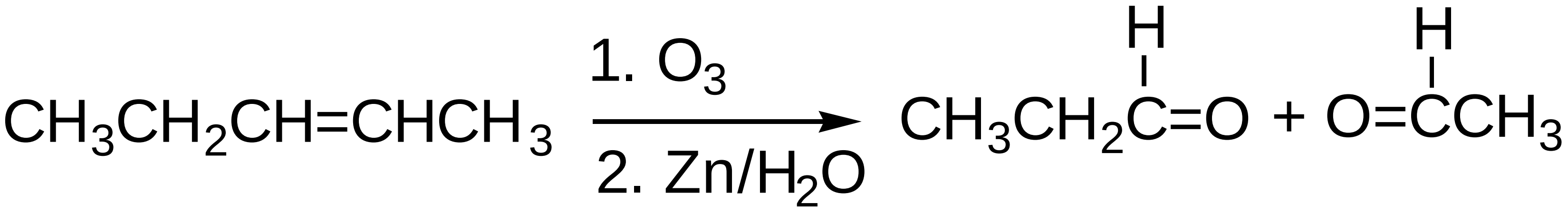
or OsO_4

a glycol

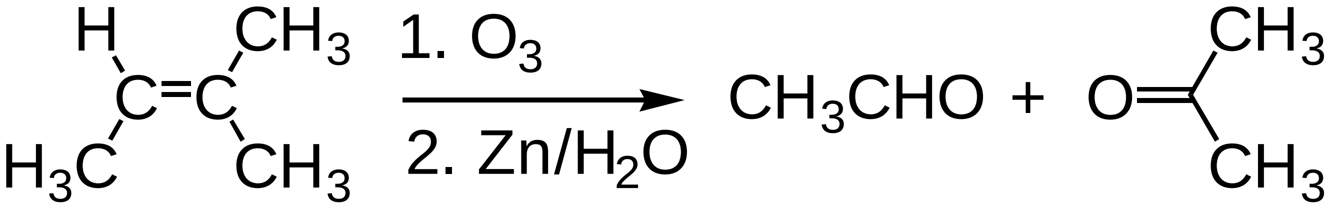
OZONOLYSIS


+ O_3
O
O
O
molozonide
O
+O
O
-
O
O
O–O
ozonide
H_2O/Zn
O
O
aldehydes and ketones

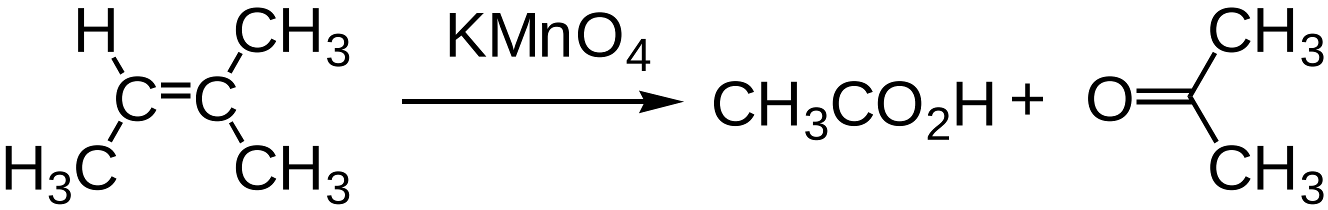
OZONOLYSIS



$$CH_3CH_2CH{=}CHCH_3 \xrightarrow[\text{2. Zn/}H_2O]{\text{1. }O_3} CH_3CH_2\overset{\overset{\displaystyle H}{|}}{C}{=}O + O{=}\overset{\overset{\displaystyle H}{|}}{C}CH_3$$

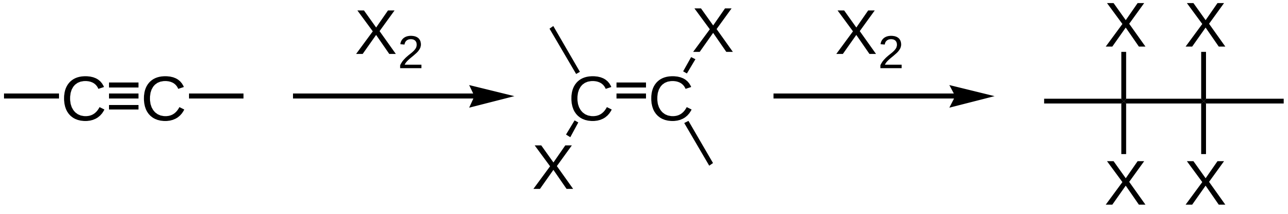


KMNO$_4$ OXIDATION

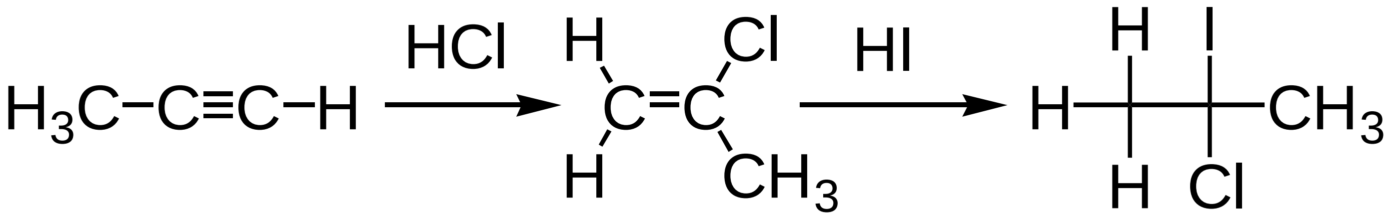


$$CH_3CH_2CH{=}CH_2 \xrightarrow{KMnO_4} CH_3CH_2CO_2H + CO_2$$

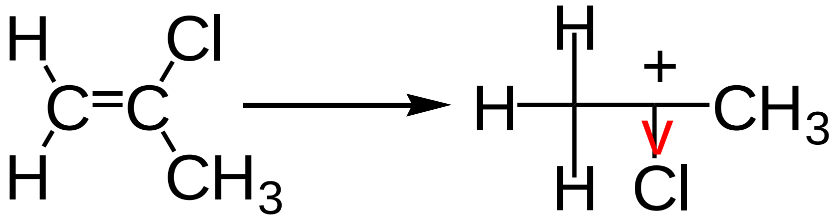
ADDITION OF HALOGEN TO ALKYNES



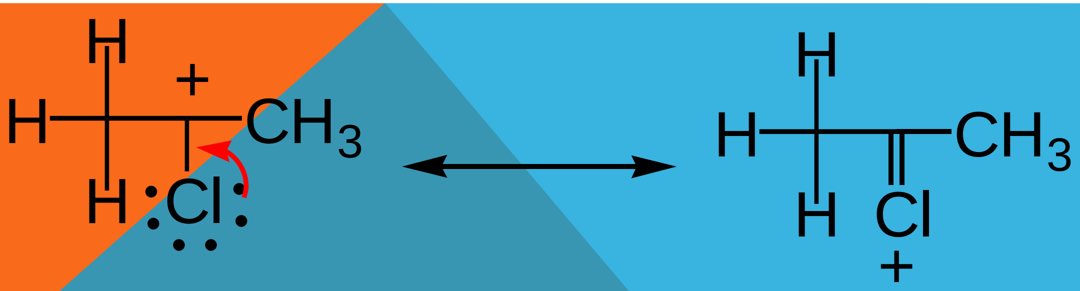
ADDITION OF HX TO ALKYNES



Does this seem reasonable?



This carbocation should be destabilized by the inductive effect of the Cl!



The cation is stablized by resonance! Remember this in CHEM 263